جامعة أم القرى
كلية العلوم التطبيقية
قسم الكيمياء

دراسات فيزيائية كيميائية على بعض متراكبات الالچينات الايونوتروبية الچيلية لأيونات الفلزات الثنائية التكافؤ



رسالة مقدمة من

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كجزء من المتطلبات للحصول على درجة الماجستير في الكيمياء

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صفحة المشرفين

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صفحة المحكمين

قرار لجنة التحكيم

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لجنة الحكم والمناقشة:

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عميد الكلية

الملخص العربي

تتكون الرسالة من أربعة أبواب رئيسية وهي :-

الباب الأول .يتضمن مقدمة عن خواص مترا كبات الألچينات الفيزيائية والميكانيكية والضوئية . كما يتضمن عرض شامل لماتم دراسته لمتراكبات الألچينات بالإضافة إلى الهدف من هذا البحث.

أما الباب الثاني فيركز على الخواص الفيزيائية والمورفولوجية للمتراكبات الچيلية الأيونوتروبية للفلزات الثنائية التكافؤ التالية Pb , Sn , Hg , Zn , Cd . ويتضمن أيضا تحضير المحاليل الالكتروليتية للفلزات الأيونية وتحضير المتراكبات الچيلية الأيونوتروبية بصور متعددة ككريات أو أعمدة أو أغشية أو حبيبات . ويشمل أيضا الدراسات الفيزيائية للكريات مثل المحتوى المائي، الحجم، نصف القطر، المرونه والشفافية . ومن خلال النتائج وجد أن المحتوى المائي يزيد عن ٩٥ % من وزن القطرة وأن متراكب Pb أكثر مرونة من بقية المتراكبات . و أن نصف القطر يزداد في هذا الاتجاه: Pb < Zn < Cd < Hg < Sn .

ومن التحليل العنصري لهذه المتراكبات وجد أن هناك توافق بين النتائج المعملية والنتائج النظرية . أما انحراف أشعة X يبين أن هذه المتراكبات غير متبلورة . وأثبتت الأشعة تحت الحمراء أنه يحدث ترابط ليجاندي بين المجاميع الوظيفية COOH ، OH وبين الأيونات الفلزية . أما الدراسة المورفولوجية بالميكرسكوب الضوئي أظهرت أن المقطع العرضي يتكون من ثقوب منتظمة الشكل متساوية القطر ، أما المقطع الطولي فيتكون من أشكال انبوبية منتظمة ومتوازية وبالنسبة للدراسة بالميكرسكوب الالكتروني فأوضحت ترتيب الشبكة الداخلية والاتجاهية على جدران الأنابيب .

وبالنسبة للباب الثالث فيتضمن الدراسة الحركية للمتراكبات الچيلية الأيونوتروبية للفلزات الثنائية التكافؤ التالية Cd , Sn , Hg , Pb وذلك في شكل كريات عن طريق دراسة التغير في كثافة الالكتروليت وذلك نتيجة للتبادل بين أيون الصوديوم والأيون الفلزي . ووجد أنه بمجرد تلامس قطرة الألچينات مع سطح المحلول الالكتروليتي يتكون غشاء رقيق حول القطرة ونظرا لأن كثافة قطرة الألجينات أقل من كثافة الالكتروليت فإنها تطفو أسفل سطح المحلول لفترة محددة تعرف بزمن الاسترخاء والتي تختلف من الكتروليت لأخر . وتحدث بعد ذلك عملية التبادل الأيوني حيث تتحول الألچينات من صورة المحلول إلى الصورة الچيلية .

ونتيجة لتكرار عملية التبادل يتكون المتراكب الچيلي مع تكوين أغشية رقيقة متعددة ومتراكمة وعندما تصل كثافة القطرة إلى قيمة أعلى من كثافة الالكتروليت تبدأ القطرة بالنزول داخل المحلول الالكتروليتي بسرعة تعجيل يمكن حسابها . تعتمد كلا من فترة الاسترخاء وسرعة التعجيل على طبيعة الأيون الفلزي ، والكثافة ، والرقم الهيدروجيني،وتركيز كلا من الاكتروليت والالچينات . وبحساب معدل تكوين الجل لكل متراكب وجد أنه يزداد بانخفاض تركيز المحلول الالكتروليتي وعلى العكس تماما فانه يزداد بزيادة تركيز محلول الألچينات.

ويتضمن أيضا حساب الدوال الثرموديناميكية مثل طاقة التنشيط ، والانثالبي ، والانتروبي ، والطاقة الحرة . ومن خلال النتائج وجدأن هناك تشابه في ميكانيكية تكوين الچل .

ومن خلال الدراسة لوحظ أن كثافة الالكتروليت أو الألچينات ليست هي المسؤلة فقط عن زمن الاسترخاء فأمكن افتراض معادلات رياضية لمعرفة عوامل الانتشار التي تؤثر على هذة الدالة .

أما الباب الرابع فيوضح دراسة كينيتيكية وميكانيكية التحول الچيلي لبعض المتراكبات الچيلية الأيونوتروبية للعناصر الثنائية التكافؤ التالية Zn , Cd, Pb باستخدام التغير في تركيز الالكتروليت مع مرور الزمن .

وتحت الظروف المعروفة pseudo order حيث يكون تركيز الألچينات أكبر بكثير من تركيز الألكتروليت . ومن خلال النتائج لوحظ أن الميكانيكية تمر بمرحلتين إحداهما سريعة ونقص التركيز فيها عالي وفي فترة زمنية قصيرة، بينما الأخرى بطيئة ونقص التركيز فيها منخفض وفي فترة زمنية طويلة . وبحساب معدل التفاعل في كل مرحلة ومن ثم حساب معدل التفاعل الكلي وجد أن التفاعل ثنائي الرتبة ولكنه أحادي بالنسبة لتركيز كلا من الألچينات والالكتروليت ومن خلال النتائج وجد أن معدل سرعة التكوين الچيلي تقل في هذا الاتجاه Zn > Cd > Pb . ومن العوامل التي تؤثر على سرعة التفاعل القطر الأيوني لأيون الفلز وكثافة الالكتروليت .

ذكرنا سابقاً أن كيناتيكية التفاعل تمر بمرحلتين إحداهما سريعة والتي يتكون خلالها الغشاء الأولي ، أما الأخرى بطيئة والتي ترجع إلى تماسك الغشاء المتكون والذي يعتمد على تركيز الألچينات ودرجة الحرارة .

ومن خلال حساب الدوال الثرموديناميكية وأيضا من خلال رسم العلاقة بين الانثالبي والانتروبي وجد أن هناك تشابه في ميكانيكية تكوين الچل .

ويتضمن هذا الباب أيضا كيفية الارتباط بين المجاميع الوظيفية في الألچينات COOH ,OH وبين الأيون الفلزي حيث يكون الارتباط إما من خلال سلسلة واحدة أو سلسلتين متوازيتين في الألچينات ويتوقف ذلك على طبيعة الأيون الفلزي .

Arabic Summary

Umm Al – Qura University
Faculty of Applied Sciences
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Physico –Chemical Studies On Some Cross-Linked Divalent Metal Alginate Ionotropic Gel Complexes

By

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A thesis

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Master Degree in Chemistry

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TO
MY PARENTS,
BROTHERS AND SISTERS

I dedicate this work to my parents to whom I owe my life and present career .

On initiative of their high spirited personality I was led to the research career .

Also to my brothers, sisters and the spirit of my grand father.

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CONTENT

Chapter I : Preface .

Chapter II : Physical Properties , Characterization and. Morphology .

of Capillary Ionotropic Polymembranes .

CHAPTER I

Preface

I . Preface :

Thomas Graham is the creater of the term "gel" . Jordan[1] began the survey on the gel structure reporting that ,"it is colloidal state," the form which is easier to recognize than to define. As with so many colloidal systems no clear-cut line of demarcation exists between gels and pastes, nor between sols and colloidal solutions, on the one hand, and gels and pastes on the other.[2,3]

Generally, gels are colloidal systems of semi-solid character, in which the colloidal particles are usually interpenetrated by liquid system. If this liquid is entirely removed, the gel formed will be called xerogel. Therefore, the term gel is assigned to systems characterizing by the following features:

a) They exhibit mechanical properties characterstic of the solid state.

b) They are coherent colloid disperse systems of at least two components.

c) Both the dispersed phase and the dispersion medium are continuously extended throughout the whole system.

Point (b) is not a criterion based on phenomenology but refers to the structure which can not be recognized at the first sight . Nevertheless, it seems desirable to add this criterion to the definition of gels . This is because a number of systems conforming with (a) and (c) but not conforming with (c) through ultramicroscopic observations. Hence, these systems can not be considered as gels.

I-1.Phase Classifications of Gels:

The gels of colloidal systems exist in macromolecular and association colloids may be grouped into three categories as follows:

a - Macromolecular gels which are preferably considered as two – phase system :-

They are consisting of a cohering mass of highly dispersed flocculation aggregates

b –Macromolecular gels in which one inclines more than one- phase concept :-

In other type of gels particularly no macromolecules are present as free kinetic units, as they all form a coherent network throughout the whole system. As the order of magnitude of the discontinuities in these gels is very small, it seems presumable that the one – phase concept is here already much more preferable than the two-phase concept. The gel could for instance be considered as a crystalline phase with very extensive lattice disturbance.

c - Macromolecular gels which are preferably considered as one – phase system :-

Here , the single macromolecules, though for the greater part of their length freely dispersed in the surrounding liquid, are bound together at certain points by cohesion forces or stronger chemical bounds . Though their character of independent kinetic units in thus lost , the free chain elements of the macromolecules still execute kinetic movements. As in gels of this type , even when stronger chemical bonds exist , no phase boundaries are present , they can be called one –phase gels .

Solid colloidal systems like ruby –glass (which may be considered as a solidified colloidal suspension of individual gold particles in molten glass) or like a “solid foam ”are excluded by this definition.

There is no doubt that the definition of the concept gel offered here applies to typical gels like gelatin, agar, cellulose and alginic acid which are characterized by the fact that one of the components of the system is a low molecular fluid.

I-2.General Classification of Gels :-

The ability of some colloidal substances to convert into a coherent system is one of the basis interests in the chemistry of gels. In general , gels can be classified into many categories as follows:

i-Organic and inorganic gels according to their chemical composition. Inorganic gels consist of myriads of highly hydrous or gelatinous particles enmeshed into a network or sponge structure in which both the solid and the liquid phases are continuous such as chromic oxide , silica and manganese arsenate. Organic gels such as gelatin , agar and alginate are assumed to consist of small anisotropic, crystal-like, molecular aggregates which retain their identity even when the substance goes into colloidal solution.[4~6]

ii-Hydro-and organogels according to the liquid phase (gels with water as a liquid component are termed hydrogel, whereas the gels containing an organic solvent as liquid are called organogels). Removal of all water from gels causes them to lose their absorbing power for liquids and vapours, as a result of coalescence of particles and the consequent decrease in porosity. There is another type of gels called "aerogel". This type of gels is formed when the liquid is displaced successively by liquids that are completely miscible with the proceeding and succeeding one (e.g.

water, alcohol, or water, alcohol and ether) the last one having a low critical temperature. The resulting jelly is then placed in an autoclave with an excess of liquid and heated above the critical point . On allowing the gas to escape , a coherent expanded aerogel is obtained.

iii-Hetero – and isogels according to the particle size (this type of gels was introduced by Ostwald) .

iv-Colloidal and coarser gels according to their framework, the former such gelatin, agar and alginates, whereas the latter such as silicates.

v-Elastic, rigid and thixotropic gels according to their mechanical properties. Gels of inorganic substances are rigid or non-elastic, whereas that of organic character are elastic and characterized by perfect elasticity through certain narrow limits and by retaining their elasticity and coherence on drying .[3]

vi-Thermoreversible and thermoirreversible gels. The former such as gelatin, agar and methyl cellulose in water. The latter such as alginates and pectates which are called ionotropic gels.

vii-Swelling and non – swelling gels depending on their abilities to swell in different solvents .

viii-Macromolecular and non-macromolecular gels depending on the length of their chains ,i.e. the molecular weight.

I-3.Formation of Gels:-

Gels may be formed either from a solution or from a solid substances (xerogel) exhibiting swelling power . The latter instance is confined to macromolecular substances. No such restriction exists for the formation of gels from solutions which are formed by reducing the solubility of the colloidal material to an extent sufficient to enable the particle to link together in some manner. This takes place by cooling (or less frequently by warming the sol), by addition of a precipitating liquid or addition of salts. This formation may be summarized as follows:-

i) Coagulation or decreasing the solubility.

ii) Chemical reaction between two concentrated solutions.

iii)Gelation of colloidal solution.

v) Swelling of xerogels.

At the beginning of the experiments, the solution from which the gel will be formed may be either colloidal solution of a macromolecular substance e.g. sodium alginate, sodium pectate and carboxymethyl cellulose (polysaccharides)or an ordinary solution of a low molecular substance such as silicic acid gels . Two fundamental conditions must be fulfilled for the gels to be formed from solutions:

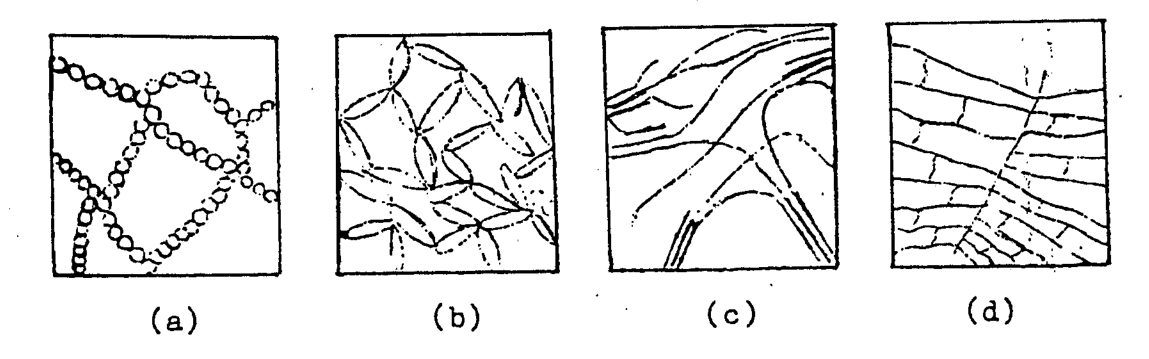
1-A solid substance separates from the solution in a finely dispersed colloidal state .

2- Separated solid particles join together to form a continuous coherent frame-work throughout the solution .

The process capable of separating (semi-solid phase), either crystalline or amorphous from a solution (or a melt) may produced a gel by introducing a condition of super saturation either by evaporation (addition of another substance

such as a non-solvent or a salt) or by a chemical reaction occurs as the first step . Secondly suitable conditions allowing the formation of a continuous framework must be realized.

A schematic picture of four different possibilities concerning the nature of the framework of the gel is shown below:



(a) Shows a gel structure consisting of sphericales (droplets) adhering to each other.

(b) Shows a gel structure of rodlet shaped particles building up a similarframework.

(c)Shows a gel structure of linear macromolecular chains adhering to each other with crystalline junction points.

(d) Shows a gel structure formed by chemical cross -linking of dissolved linear macromolecules.

It can be seen that, the conditions favouring the decrease in the solubility of the colloidal material to an extent enables the particles to link together forming a coherent continuous framework structure, are those producing gels. Such conditions can be summarized in the following aspects:

a- Variation of Temperature:-

Certain substances like gelatin and agar are capable to swell in water at ordinary temperature but are not peptized to form sols until the temperature is

raised. Cellulose acetates behaves the same way in benzyl alcohol. At higher temperatures, the liquid phase serves the double role of peptizing agent and dispersing medium. On cooling a such sol system, a jelly results provided that the concentration is suitable.

With solutions of many colloidal materials, particularly linear-polymers, the position is rather different . Many of these polymers appear to show either a negligible or an infinite solubility in a given medium. The changeover from one extreme to the other can often be affected by alteration in the temperature or composition of the medium, and when this leads to a reduction in solubility, the phenomenon of gelation is frequently observed.

Gelatin, for example, disperses readily in hot water, giving what is probably a molecular solution , and on cooling to room temperature this sets to a clear uniform gel (if the concentration exceeds Ca. 1 percent).

Non-aqueous gels are often prepared by cooling sols of suitable strengthes. The gels given by a few percent of aluminium fatty acid salts such as the stearate, oleate or naphthalene, in hydro carbon media are well known , and frequently very stable.

Generally an elevation of temperature hinders gelation, provided irreversible chemical changes do not occur then in a system because the micro-Brownian motion of segments becomes more intense and the number and lifetime of bonds between macromolecules consequently decrease. Conversely , a drop in temperature promotes gelation because the spectrum of contact between macromolecules, then, expands and shifts toward higher strength. The sol-gel transition, like the gel-sol transition, occurs continuously with change in temperature in thermo gels, but not the same in ionotropic gels.

Sometimes, heating promotes gelation, conversely , cooling causes the liquification of a system such as methyl cellulose in water and cellulose nitrate in ethanol. Again , the greater the concentration, the higher is the temperature at which solutions of macromolecular substances becomes gels.

b -Salting out and pH controls :-

The salting out process is carried out by adding salt solution or a solution of a mixture of salts to a sol of colloidal solution or sols . This can lead to produce a variety of effects including gel formation by neutralizing the sol particle charges through reducing the zeta potential(φ)depending upon the particular system.

Loeb[4] found that the swelling approaches a minimum value at the isoelectric point, and increases on neither side of pH 4.7 during the investigation of the effect of pH and salts on swelling of gelatin.

The temperature of gelation of gelatin sol is influenced by the pH and by the presence of neutral salts . Pectin jellies are usually obtained in acid solutions containing sugar. If alcohol or glycerol is substituted for sugar, jellies will form in the absence of acid[8] and they made in alkaline solutions[9]. On the other hand , alginate jellies are obtained in only acid solutions[9,12].

The pH of a solution greatly affects the gelation ability of aqueous solutions of amphoteric macromolecular electrolytes such as proteins. [13]. Gelation occurs best at pH values which correspond to the isoelectric point because the number of oppositely charged ionized groups along the length of a molecular chain is the same, and this helps to establish bonds between macromolecules . As pH changes towards either side of the isoelectric point, macromolecules assume a charge of the same sign and this hinders the formation of bonds between them. When a large

amount of acid or alkali is added , the extent of ionization of inorganic groups decreases and the tendency to gelate increases again.

Aqueous dispersion can , however , be affected by salts even in the absence of chemical reactions . With the extreme type of hydrophobic suspensions quite a low concentration of an indifferent salt brings about coagulation , and the gel formation is seldom or never observed , largely on account of the low concentration of disperse phase (of the order 0.1 percent) . However , in more hydrophilic suspensions , e.g. aluminum and ferric hydroxides , bentanite , etc., so the amount of dispersed material can be increased , and the gels can frequently be obtained by suitable addition of salts , usually about one-half of the amount needed for complete precipitation . Thus with the positively charged hydroxide sols , divalent ions such as SO_4^{2-} are much more potent than the univalent such as Cl^- . The gels so formed are frequently thixotropic in behaviour , and this forms the standard method by which such gels are produced .

The extreme type of hydrophilic suspensions , e.g. gelatin and proteins are only affected by high salt concentrations due to the salting out effect.

Gelation of sols of gelatin and other ionogenic water- soluble polymers is very dependent upon the pH as well as the nature and concentration of the salts present.

c- Chemical Reactions :-

The rapid throwing out of large amounts of materials by chemical reaction lead to gel formation, e.g. barium sulphate gels from saturated solutions of barium thiocyanate and manganese sulphate. Substances which tend to separate as amorphous precipitates frequently give gels when first formed, the hydroxides of aluminium, iron and silicon being good examples.

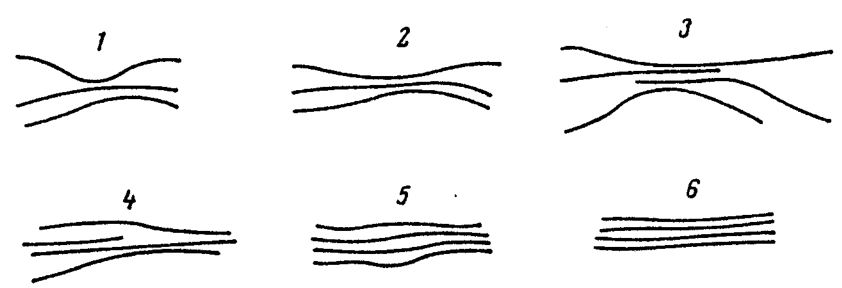
d- Chemical Crosslinking of the Macromolecular Chains in Colloidal Solutions :

The forces causing interlinking of the particles in the gels may of various nature , comprising ordinary cohesive forces (van der Waals forces), polar forces , heteropolar and homopolar valency bonds foreign atoms or molecules may participate in the formation of the links beside the direct material contact between the particles. In a number of cases , bridges formed by tightly bound water molecules as in poly- saccharides are observed.

Generally , gelation occurs because bonds originate between polymer molecules which are kinetic units in a solution . These bonds can exist for a short time , causing the origination of associates . However , if the average lifetime of bonds between macromolecules is very long (practically infinite) , the formations do not disintegrate and to a certain extent exhibit properties of a solid phase . Permanent bonds may originate between molecules in solutions of polymers as a result of interaction between the polar groups of macromolecules or between ionized ionogenic groups bearing electric charges of opposite sign . Sometimes chemical bonds are formed between macromolecules , e.g. , when rubber is vulcanized in a solution.

Thus , gelation is the formation and gradual strengthening of a three-dimensional network in a system . When solutions of macromolecular substances become gels , bonds are formed not only at the ends of kinetic units, as is the case when lyosols having elongated rigid particles become a gel , but between any regions of flexible macromolecules as long as they have groups which may interact with one another .

Individual regions of molecules that interact with one another become ordered when a gel is being formed .i.e., they orient parallel to one another because this reduces the free energy of a system . The degree of orientation depends on both the nature of a macromolecular substance and gelation conditions . The below figure schematically illustrates various types of orientation of macromolecular regions in a gel , which are arranged in the order of their increasing strength .



Types of contacts of macromolecules in a gel (arranged in the order of the growth in their strength)

There is a continuous transition from the simplest point contacts between macromolecules to crystallites , i.e., regions having an ordered crystalline structure . Since contacts may be of the most diverse nature in the same gel , it is expedient to use the concept of spectrum of molecular contacts for a given gel . This spectrum can be represented by a distribution curve which characterizes the fractional composition of contacts either by their strength or by their dimensions .

It is very likely that not only individual molecules , but also their bundles , can be structural units of the three-dimensional network of gels . Unfortunately , this so far and has not been studied at all .

If the bonds between macromolecules are not too strong , mechanical action (stirring or shaking) can destroy the structure and a gel (just as a colloidal gel) becomes a liquid . When the external effect is eliminated , the solutions obtained may spontaneously gelate again . But when molecules are combined into a continuous three-dimensional network by chemical bonds , strong mechanical effects irreversibly destroy a gel .

I-4.Changes Occurring During Gel Formation:-

A good deal of information about the structure of gels has come from the study of the physical changes which occur in sol-gel transformation .[14]

a-Thermal:-

The cooling curves of solution of low molecular weight substances usually show pronounced breaks or arrest points when solute begins to separate. With sols, the onset of gelation produces a small but definite arrest , showing that the sol-gel change is accompanied by liberation of heat , i.e. , by a diminution in heat content for thermogels .

With thixotropic gels any thermal affects in the sol-gel transformation appear to be negligible, a not surprising result in view of the small amount of mechanical energy required to bring about liquification.

Again , with ionotropic gels such as alginates , the sol-gel transformation are irreversible , therefore , the increase of temperature does not cause liquification.

b -Electrical Conductivity :-

Changes in electrical conductivity during the formation of a gel appear at the first sight to be remarkably small in relation to the enormous increase in the viscosity .[15] Thus with iso –electric gelatin the conductivity decreases by

only a few percent . The transition from sol to clear jelly with soaps , no measurable change in electrical conductivity is observed , although a marked fall is found when the further change to the hard , opaque "curd" state occurs . This behaviour was attributed to the nature of the gel structure .

If the sol contains electrolytes , the conductivity changes during gelation are usually negligible . The slight increase observed in some cases being ascribed to a secondary effect . The decreased ionic adsorption on the colloidal is arising from its aggregation .

Another rather striking result is that the electrical mobility of solid colloidal particles as quartz , suspended in a gelatin sol is unaffected by gelation at any rate in the weaker gels .[16] This shows , that the gel structure must break down and reform extremely readily , a type of micro- thixotropy .

I-5. Mechanical properties :-

These naturally obvious changes in the sol-gel transformation . Coinciding with the marked increases in viscosity come the development of elasticity or plasticity , properties charactestic of solid bodies .

The viscosity provides a simple way of detecting the onset of gelation , but the interpretation of such measurement is not easy , since non-Newtonian flow or "ana- malous viscosity " is invariably present during sol-gel transformation . Nevertheless sols much as those of gelatin , agar and nitrocellulose show an increase in viscosity , suggesting that the two are intimately related.

The development of elastic properties during the change from sol to gel does not in general occur sharply , and elasticity has been detected in the sol state close to the transition point , particularly with gels of agar , gelatin polysaccharides

and other polymers . The elasticity depends very largely upon the rate of relaxation of the gel structure in relation to the time for the necessary measurements .

The sharpens of the sol-gel change , which will be reflected in the development of elasticity will also be affected by the degree of homogeneity of the gelling agent , particularly as regards chain –length in case of polymer . In general , the shortest-chain members tend to have the greatest solubility and the wider spectrum of chain-lengths the more diffuse the transition from the sol to the gel state .

a -Elasticity , Rigidity and Thixotropy:-

The most interesting properties of ordinary gels are their mechanical characterstics, , particularly elasticity and rigidity . Solutions of polymers having extremely weak intermolecular bonds are capable of flowing , i.e., they react even to very weak shearing forces . But if the lifetime even of some contacts between macromolecules is very long , a gel becomes capable of resisting flow up to a definite value of shearing stress and acts as an elastic solid under shearing conditions below this critical value. The value of critical shearing stress depends on the number and strength of molecular contacts.

The mechanical properties of gels are strongly affected by their concentration . Gels containing a small number of permanent intermolecular bonds per unit volume are very elastic . Conversely , gels having a large number of bonds between macro- molecular are rather poorly elastic because the greater the number of bonds between polymer chains , the less is the possibility of a change in the shape of macro- molecules ,i.e., the more rigid , is the network formed .

In agar, the critical stresses is usually increased very rapidly with concentration . A system exhibits gel properties when the content of material in solution is very low , i.e., the system is non-fluid.

At temperatures which are higher than the temperatures at which a gel "melts" neither diluted nor concentrated gels exhibit shearing stress. Non-gelating solution, such as solutions of cellulose nitrate in acetone , do not exhibit critical shearing stress at any concentrations . They flow at the lowest shearing stress although very slowly because of their high viscosity .

Relaxation processes in gels occur at a higher rate than in polymer solution because only individual , comparatively short chain segments can move in gels. Therefore , the elasticity of gels is always more pronounced than that of cross-linked solutions as metal - alginates .

Hysteresis phenomena or permanent deformation are commonly observed , particularly at the higher deformation and longer times . For example with gelatin gels , it observed that the reversibly elongated and irreversibly compressed cylinders the tensile strength is a minimum in the direction of the axis , but with irreversible elongated and reversibly compressed cylinders it was a minimum in directions perpendicular to the axis .[19] The direction of minimum tensile strength during irreversible deformation showing that some rearrangement in structure . Thus occurred if the gel possesses a fibrillar structure. [20]

Generally , the study of elasticity under varying conditions is clearly a fundamental method for elucidating the structure of the gel .

If a suitable amount of electrolyte is added to a fairly strong sol (in case of inorganic gels such as ferric oxide , chromic oxide or stannic oxide) and the mixture is allowed to stand quietly , it will set to a jelly which is no more cloudy

than the original sol . If the resulting jelly is then shaken , a sol is re-formed which will set again on standing , and the process may be repeated as often as desired . This isothermal reversible sol-gel transformation has been termed thixotropy.

Some polymer gels such as gelatin possess well defined "thixotropic" properties. [21] The strength of the bonds between the macromolecules of these gels should be sufficiently low so that they could easily be destroyed under the action of sheering force . Moreover , such gels have a sufficiently narrow spectrum of molecular contacts do not exhibit thixotropy . When the structure is being destroyed by mechanical action , most of bonds are cleaved if the spectrum of molecular contacts are narrow . This is the essence of thixotropy . Thixotropy is exhibited only under special conditions which favour to narrow down of spectrum , e.g., on considerable dilution or at the initial stage of gelation when structures are not yet formed from oriented macromolecular parts.

b - Memory :-

A peculiar property of gels is their "memory" of how they were formed . Suppose one gel was prepared from a dilute solution and the other from a concentrated one . Then , the gels were dried at low temperature to the same moiture content and were allowed to swell in water . As a result the first gel would swell much more than the second one because their internal structure , which originated when they were, formed , was preserved to a certain extent when they were dried .

c-Syneresis (Aging):-

Aging signifies the changes in properties which a freshly formed gel undergoes on standing . Whereas syneresis refers to the spontaneous concentration

of a gel with liberation of the dispersion medium (usually water) . This is not the dehydration occurring upon drying , but it takes place also in moist air and at low temperature . The extent to which syneresis occurs depends upon the system , but in general it decreases with increasing the concentration of gelling agent .

The occurrence of syneresis may show that the original gel is thermodynamically unstable , but the absence of a such syneresis does not prove the converse to be true , owing to the time lags so common in the gel systems .

Concerning the ionotropic metal alginate gels , the syneresis is so slow and the gels are more stable thermodynamically owing to the strength of chelation between the chelated metal ions and the carboxylate and hydroxyl functional groups of alginate macromolecular chains .

d-Swelling :-

Practically all substances which form the so-called elastic jellies will swell in a suitable liquid or in the vapors of such liquid . Thus dry gelatin , fibrin and starch will swell in water at ordinary temperatures , forming jellies that are peptized at higher temperatures to give sols . Albumin swells in water but not in alcohol , benzene, or ether . Vulconized India rubber swells in various organic solvents such as benzene, toluene and xylene but not in water ,soaps swell in water; as well as in many organic solvents .

Some substances like gum Arabic swell continuously at ordinary temperatures until the entire mass is peptized to give a sol , whereas others like gelatin and rubber approach a maximum of swelling without sol formation. [22,23]

On the other hand ionotropic gels like metal alginates will swell or shrink in water and most organic solvents but not peptized at higher temperature ,i.e. not form sols .

The pH and added salts will affect the swelling property to a large extent. [22~24]Procter and Wilson [22,23] applied Donnan's theory of membrane equilibria in interpreting the effect of pH on the swelling of protein jelly . The application of a such theory to the swelling of gelatin is certainly a step forward in explaining the mechanism of the swelling process , although it is not helpful in interpreting the swelling of rubber in organic liquids or the swelling of isoelectric gelatin. [25,26]

Ultramicroscopic examination has been much used to indicate whether aggregation occurs during transition from sol to gel , the chief handicap being the small difference in refractive indices between the disperse phase and dispersion medium in the lyophilic systems as in the present work . This means that the resolving power is unlikely to approach the fine structure which is existed in most gel systems .

Sols of thermo-reversible gels such as gelatin and agar show few particles in the ultramicroscope , but during the transition to gels many more particles appear , these being in Brownian movement until stopped by gel formation . No continuous "net" structure is seen and the scattering particles apparently remain separated. An increase in aggregation during gelation leading to more ordered arrangements and ultimately to crystallization , which can be shown by x-ray diffraction pattern.

On the other hand , sols of non thermotropic-irreversible gels such as alginate , the sol-gel transformation depends on the direction of interdiffused metal ions .

In general the extent of swelling depends on the following factors :

1) Nature of solvent .

2) Degree of crosslinking .

3) Nature of fixed ionic groups .

4) Nature of counter ion

5) Concentration of the solution .

6) Ion-pair formation and association .

7) Capacity for ion exchange .

e-Volume:-

The solution of a lyophilic colloid frequently produces a marked volume contraction . Generally , the formation of gel from sol also produces a volume change . This change may be positive , zero or negative depends on the nature of sol-gel transformation . These volume changes have frequently been attributed to changes in hydration. (17)

The volume changes are clearly very small and much less than the contraction observed when lyophilic colloids swell or dissolve in water , which for methyl cellulose and gelatin are of the order 6 - 8 c. c per 100 gm solid . The volume change in gelatin (an expansion) is initially very marked , then slows down , but is still alternating even after six months . It is evident that the processes responsible for the volume change and gel formation continue , even in the stiff gel state .

True solutions of high polymers shown to possess elastic properties , although the relaxation times are much less smaller than for the common gels. (18)

I-6. Optical Properties :-

Gels as normally prepared are usually , although not invariably optically isotropic , but become doubly refracting when suitably stressed as elongation ,

compression, or shear . This gives rise to the so-called "photo-elastic " effect which can be observed in various way , but usually under crossed Nicols .

Gels are widely used for the photo-elastic study of stress patterns in engineering problems . Attempts have been made to use photo-elasticity of dilute gels as a means of following their relaxation under stress but with a great caution .

a-Orientation:-

In anisotropic gel , the anisotropy is invariably due to an orientation of the elements building up the framework structure . Anistropy may reveal itself in various ways , as e.g. in the form of anisotropy of swelling , anistropy (birefringence) , or mechanical anistropy .

The relative change of linear dimentions upon swelling or contraction , the refraction or absorption of light and the stress strain relations are then found to be different in different direction . If crystallites are present , orientation can be read from x-ray diffraction pattern . The majority of gel-like macromolecular systems is anistropic. Orientation is due to the activity of the living matter , or by which they have been formed . The birefringence can be shown by the polarizing microscope .

Anistropic gels produced in the laboratory own their orientation of a previous deformation . This may be either effected by mechanical deformation of an isotropic gel or by preventing the gel from isotropic contraction , for instance during drying . In both cases the random orientation of the structural elements of the framework is changed into a more or less preferred one in one or two directions of space .

If the molecules are , as a rule optically anistropic particles , since the polaris- ability is different in various directions , except in a few cases . Systems

consisting of oriented molecules , like crystals , will therefore , be optically anistropic except regular crystals which contain isotropic molecules isotropically arranged in space .

If isotropic molecules are anisotropically arranged in space , in that the intermolecular spacings are different in different directions , the system will exhibit optically anisotropic too . Such anisotropic arrangement may for instance ensure from a mechanical extension or compression in one direction ore some other forms of mechanical distortion . A regular crystal , when stretched in one direction becomes birefrigent .

Other forms of anisotropic spatial arrangement of structural element , which are themselves isotropic are very important .

b-Birefringence in Swollen gels :-

The birefringence phenomena is due to orientated structures of a special kind of gels . A system of parallel rodlets or platelets embedded in a medium of different refractive power gives rise to a double refraction , even if the rodlets or platelets themselves are isotropic . Instead of discriminating rodlet and platelet birefringence , it is preferable to simply take the sign of the birefringence as a criterion , since oblong lamella , orientated with their longest axis in one direction , will also give rise to the same sign of birefringence as rodlets orientated in that direction , and etc. Rodlets orientated in parallel planes will yield the same type of birefringence as platelets orientated in parallel planes .

Structural birefringence has been met with in various typical orientated gels , e.g. in gels of gelatin [27] , cellulose [28] ,cellulose [29] nitrate , muscle

myosin[30] , alginate and various objects of biological origin. [31] It demonstrates the presence of orientated polymolecular anisotropetic particles .

I-7. General Survey On Alginate Chemistry

I-7.General survey on Alginates Chemistry :-

Sodium alginate is the starting material of the present work . Alginic acid is naturally occurring carboxylated polysaccharide. [32~35] It is a binary heteropolymer containing 1,4-linked α-L-guluronic acid and β-D-mannuronic acid units of varying proportions arranged in a liner block copolymer structure .[36~39] It found in brown seaweeds whose chemical formula is. [37,40]

Structure of alginic acid

It is commonly obtained from macrocytis Pyrifera , Laminaria and Elkonia species . The alginic acid of these species varies in the proportions from 14 to 40 % of the dry solids of these seaweeds . The alginate in seaweeds behaves as a base exchange material . The molecular weight varies between 48,000 and 186,000 [40] depending on the origin and method of preparation.

The mannuronic acid and guluronic acid units are not distributed regularly along the polymer chains so that these units can be isolated after limited degradation with acids [41~43] , free radical producing synergists such as ascorbic acid [44] and iron (II) salts [45] in presence of H_2O_2 .or by γ irradiation. [46]

Sodium alginate is soluble in water but insoluble in alcohols , ethers and in most common organic solvents and show a great adsorption capacity , while alginic

acid is insoluble in either water or organic solvents . It is a weak acid which displaces CO_2 from carbonate solution and resistants to hydrolysis. [47] Solubility of sodium alginates depends on the source and Ph. [45]

The ionization constant of alginic acid exhibits the highest pK values for highest proportions of guluronic acid units . The pK values were found to be 3.38 and 3.65 for mannuronic and guluronic acid units , respectively. [42,49]

Moreover , it has been found that alginic acid takes up 5.4 mequiv. Na+/g at pH 3.3 and the pK is 2.93 at 25 °C. [50]

Alginate owes much of its commercial importance to its ability to form very viscous solutions . Apparent intrinsic viscosity was found to be about 17.1 , 18.5 and 19.3 dl / g for soluble fractions , the unfractionated and insoluble fractions of alginates , respectively. [51] Heating the alginate solutions for about 15 min at 120°C altered the intrinsic viscosity to about 5.5 dl/g . [41]

The fractionation of alginic acid leads to the separation of the two fragment constituents which not only differed markedly in molecular weight , but also differ in exchange properties. [52]

Several authors studied alginic acid fibers which show a clear X-ray diffraction pattern similar to that of cellulose. [53-55] The distance along the fibers was found to be 8.7 °A .

The more common gels known till now are those consisting of more or less irregular systems of long chain molecules . Such gels are unstable and can be transformed to sols on warming such as gelatin , agar and starch ....etc . The chain molecules of these gels are held together by weak van der Waal's forces . These gels are known as thermoreversible gels .

On the other hand , sols consisting of long chain molecules carrying ionic groups , i.e. cationic or anionic are termed polyelectrolytes and can be transformed into gels by the diffusion of anionic or cationic ions , respectively. [56]

Alginate shows a high affinity for chelation with polyvalent metal ions.[57,58] This chelation is not so simple , but a sort of bridge between the carboxylate and hydroxyl groups of alginate macromolecule and the polyvalent metal ion is occurred . Schweiger [59] in his investigation for the precipitation of acetylated alginate by divalent metal ions suggested that the free hydroxyl groups are essential for the precipitation. [60] He , then concluded that divalent metal ions are bound to alginate as a complex involving two carboxylate groups of one macromolecular chain and two vicinal hydroxyl groups of another chain .

Addition of a divalent metal ion to a solution of alginate causes marked changes in properties of solution , namely an increase in viscosity , gel formation and precipitation. [61] This process is called gelation or sol - gel transformation and very important from the practical point of view .

The sequence of divalent metal ions based on both gel forming ability and gel affinity were significant different . The amount of divalent metal ions necessary to obtain precipitation of alginates was found to increase in the order [62]

$$Ba < Pb < Cu < Sr < Cd < Ca < Zn < Ni < Co < Mn < Fe < Mg$$

The ion exchange properties for gelation between alginate and polyvalent metal ions depend on the chemical decomposition of alginate , i.e. the mannuronic/guluronic acid ratio. [63] Alginates lower in mannuronic acid have a lower affinity for gelation and vice versa . This means that the affinity of alginates for divalent metal ions increases with increasing the guluronic acid residues .[64]

Ion exchange properties of alginates have attracted considerable attention owing to their bearing upon some practical uses for these materials. [65] Therefore, the relative capacity of alginates for metal ions have been studied by several authors. [56,57,59,62,66]

The exchange processes in terms of the physical properties have been investigated by Mongar et al. and were reported elsewhere [67,68]. The distribution coefficients between monovalent and divalent metal ions have been also studied as a function of pH. [49,64,69-74]

In addition to the chemical decomposition dependence of ion exchange affinity[63], the pH 's [48,62], the nature of the metal ions [69] and the concentration of these metal ions [62,75] play very important roles in the exchange processes. Thiele [56] based this fact to capillary diameters of the gel formed which increase in the order

$$Pb < Cu < Cd < Ba < Sr < Ca < Zn < Co , Ni .$$

The diameter depends to a great extent on the pH values which increases in the same order.[42,61] A such sol-gel transformation resulting from crosslinkage between the interdiffused metal ion and the carboxylate and hydroxyl groups of alginate macromolecular chains leads to an orientation of the chains and solvent molecules toward the chelated metal ion .[56,58] Thiele and coworkers studied the order of orientation of metal alginate complexes and arranged them into ionotropic series. [76,77]

Since sodium alginates show different selectivity behaviour toward the metal ions [78~80] which is unusual among polyelectrolytes and depends on the polyuronic acids ratio in the alginate sample [63,80], the selectivity coefficients of the binding metal ions has been investigated in details. The strong selective

binding is a propety of the polymer and to the physical state [79,80] (sol-gel transformation) .[9,33] The selectivity coefficients for mixtures of divalent metal ions such as Cd-Sr [39] , Ca-Sr [70] , Ca-Na [34] , Ca-Co , Mg-Sr and Mg-Ca [64,81] , have been also investigated . In general, the affinity was found to increase with increasing the guluronic acid fragment in alginate ,i.e. depends on the alginate source .

The interaction of monovalent and divalent metal ions with alginate in aqueous solutions were investigated by measuring the counterion activity coefficients. [71,72,82~85] The counter ion selectivity were measured by permelective membranes [86] , osomotic Donnan equilibria [87] and cation sensitive electrodes. [88]

Microstructure of such gels has not yet been throughly investigated . The two first attempts to study membrane ultrastructure by electronmicroscope were those of Arden [89] and Pietch [90,91] Helmcke [92] subsequently developed the carbon and metal shadowing techniques which made work exact studies possible . These studies shows that membranes are cohesive systems consisting of open-called foams , i.e. vacuoles with branched walls . Fastening the cellular network together were long hose and chain-like ribs which spread out in three dimintions . Very shortly thereafter , Moier et al . [93] and Goetz [94] conducted investigation which substained Helmek's findings . They observed further that the pore diameters bore no direct relationship to the size of the permeating substance because the former were crevice-shaped rather than circular.

However , open-called foams are by no means the only alternative available to polymeric membranes. Other possible structures are cylindrical capillaries such those found by Thiele in ionotropic gels.[66] Other earlier works on

electronmicroscopic studies of gels are not entirely reliable since speciems preparation is accompanied by artifact appearance.

Although ,the chromatographic technique is widely used for separation of most metal ions , this technique is very poorly developed for the separation of metal ions on alginate columns. (95-98) Indeed , alginate columns are used on a large scale for separation of most organic substrates such as amino acids (99), aromatic amines (100,101) and purines and pyrimidines(102) ...etc .

The electrical properties of alginate sols and metal alginate complexes were investigated. (103,105) The equivalent conductance at infinite dilution of H-Ca alginate was found to decrease with increasing the degree of exchange and reached a minimum , followed by an increasing to maximum . Solutions of metal alginates was in the order. (105)

$$Pb \simeq Zn < Ba < Ca < Cu \simeq Al < Fe < Ni < Sn$$

Moreover , the electrical conductivity under the influence of high frequencies for divalent (106-108) , trivalent metal alginate complexes and alginic acid in the column gel forms have been measured .(12) The electrical properties were found to depend on several factors such as ionic radii and polarazability of metal ions, strength of chelation between the metal ion and the functional groups of alginate and orientation property .

The oxidation of alginates by HOCl (109) or HIO_4 (110) leads to the degradation of the polymer into oxalic acid and either L-tartaric or D-tartaric acids depending on the major ratio of polyuronic acid units in the sample . The attack of the oxidat occurs on C-2 and C-3 of alginate macromolecule which considered as an evidence of the postulated structure for alginate. (36,59,60) On the other hand , the oxidation of alginates in alkaline medium of higher pH's leads to the formation of

mono-or diketo alginates. [111,112] The formation of mono-or diketo derivatives depends on the molar concentrations of the reactants as well as the pH of the medium . The attack of the oxidant is also took place on C-2 and C-3 of alginate macromolecule .

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Aim and scope

Aim and scope:-

Gelation and gels are very important in medicine and biology because plants and animals are mainly composed of gels . Again , the gelation of polymer solutions is of great importance in technological processes . The formation of glue layer in pastings , the gelation of pyroxylin and the production of artificial fibers are all gelation processes . Several processes in food and bread-baking industrials are also connected with gelation . Clean rawhide , specially prepared animal hide which does not have a hair and form leather is made in tanning , is gel .

In view of all the foregoing aspects the present work is of particular interest . Sodium alginate polysaccharide was selected from many natural polymers to its great importance and wide applications such as in medicine , food processing , agriculture , solar energy cells as well as the wide applications in analytical and preparative macromolecular chemistry . There is several thousands of patents and publications on sodium alginate and its derivatives .

The present investigations is aimed at consolidating and adequately portraying the knowledge in the field of material science with respect to the chemistry of natural polymers . It is also emphasize the dynamic aspects of the phsico – chemical properties as well as the fundamental consideration of geometrical structure , stability and basic chemical principles .

CHAPTER II

Physical Properties ,

Characterization

and Morphology .

II . 1. Introduction

II-1. Introduction :

Sol-gel transformation occurs by diffusion of polyvalent metal ions into alginate sol . The gelation process takes place stepwise by replacing the Na^+ counter ions of alginate macromolecule by the polyvalent metal ion to form an egg-box-like structure[1~3] gel complexes . It is well known that the metal ions which cross link the macromolecules are attached partially by ionic groups to the carboxylate groups and partially by coordinate bonds to the hydroxyl groups of the alginate chains. [4]

The ion exchange process depends on the nature and concentration of metal ion [5~7] , pH [8~10] and the polyuronic fragments (guluronic / mannuronic ratio) [8,11] of the alginate sample which in turn depends on the source of alginate. Guluronic rich alginates have a higher affinity for chelation with divalent metal ions than mannuronic acid rich alginate. Hence, alginates show a different selectivities toward the metal ions which is a propety of the sol-gel transformation.[12~14] Thiele [15] based this fact to capillary structure of the gel formed and arranged the gels into series .

The gel formed are ionotropic in nature which are irreversible and characterized by the orientation of the macromolecular chains and the solvent molecules toward the chelated metal ions . Thiele arranged these gels according to orientation in an ionotropic series. [16] These ionotropic gels can be formed in different shapes such as pellets , discs , membrane and columns depending on the apparatus , used. [17,18] These gels are usually optically anisotropic which characterized by birefringence caused by the orientation of the polymer units. [16,19] This anisotropy will effect the mechanical properties. [20]

The formation of ionotropic gels is accompanied by changing in the physical properties where the gel formed has a smaller volume than the original alginate solution . The greater the birefringence is the greatest the shrinkage. [10] The shrinkage and the birefringence follow the same order for the previous ionotropic series . At a certain concentration of divalent metal ion electrolytes , the viscosity reached a maximum value . The concentrations giving the maximum viscosity are increased in the same order. [10]

Since alginate owe much of its commercial importance to its ability to form very viscous solutions , viscosity studies is very important . On chelation of alginates with divalent metal ions, the viscosity goes through a maximum proceeding the onset of gel, followed by a decrease in viscosity after the formation of gel . The relation between the gel volume and the amount of polyvalent metal ions bound is complicated which depends on the total salt concentration as well the intrinsic viscosity and the source of alginate. [10,21]

The mechanical properties such as elasticity , shape , transparency and mechanical strain are very importance from the practical handling and uses of these metal alginate gels . Its affected by several factors such as the nature of metal ion , concentration of both alginate and metal ion as well as the pH and viscosity of alginate sol which depends on the guluronic / mannuronic acids ratio .

The stability of these ionotropic gels were determined from the viscosity measurements and found to be decreased in the order. [22,23]

$Ba^{2+} > Cd^{2+} > Cu^{2+} > Sr^{2+} > Ni^{2+} > Ca^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$

The transition elements of the third period show increasing of the stability with increasing atomic number $Mn^{2+} < Co^{2+} < Ni^{2+}$, while the ferrous ion is not

included because the difficulty to prevent oxidation it to Fe^{3+} ion but it may be a rank between Mn^{2+} and Co^{2+} metal alginate gels .

The influence of ion exchange on optical properties and mechanical properties for metal alginates has received a little attention. Mongar and Wassermann(24)investigated the effect of ion change process on the optical properties of sodium and calcium alginates in the fiber forms . They found that the exchange process was accompained by a loss in birefringence , by an axial contraction and by an increase in elasticity . Again , Smidsrod (25) suggested modules for the arrangement of monomers in a blockwise fashion along the chain . He attributed the mechanical properties of Ca-, Sr- and Ba-alginates according to the way of arrangements in his modules . Tempel et al. (26) studied the rheological and swelling properties of Ca-alginate using weissen berg . Rheogoniometer and discussed the results in terms of the number of statical chain elements in a sodium alginate chain . Masakatsu et al (27) investigated the rheological properties of Ca-, Sr-, Ba- and Pb-alginates in the gel rod forms, by measuring the tensile stresses under small strain and interpreted the results in terms of the number of junctions according to his modulus . Furthermore, Gemeiner and Coworkers (28) investigated the properties of Ca-alginate in the spherical form.

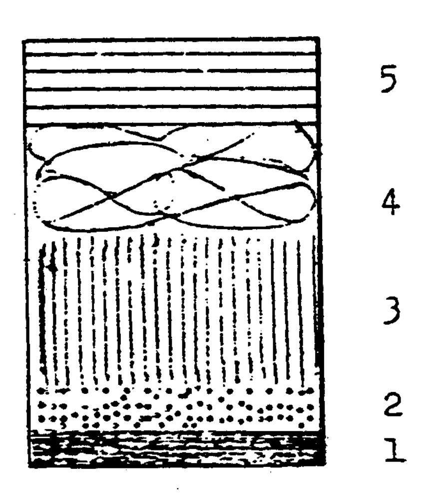
A little attention has been focused on X-ray diffraction patterns or IR of alginates and its derivatives. There is a classification of gel on the basis of the phase diagram of polymer-solvent system (29) for amorphous and crystalline polymers . One-or two-phases constituents presented were based on stability and swelling . Dolmatova (30) studied the X-ray diffraction for alginic acid , sodium alginate and calcium alginate and reported that alginic acid and Ca-alginate exhibited crystalline structures, whereas sodium alginate showed amorphous

structures . His result are not conclusive , because the X-ray diffractions were not too sharp for discrimination.

An infrared spectra were reported for alginic acid and cobalt alginates.[31] The strong band appeared at 1735 cm^{-1} was assigned to the free carboxyl group in only alginic acid , while the band at 1600 cm^{-1} was assigned to the solidified carboxyl group . In these cases , the chelating ability of the polymers were not evident for the bonding action by two vicinal hydroxyl group as reported by Schweiger.[2,22]

Microstructure investigations on metal alginate complexes is still scarce . The direction of diffusion of metal ion into the alginate sol polyelectrolyte play very important role in the structure of the gel formed . When the metal ions diffuse upward , non-capillary structural gels are formed . This method is called "ascending technique". On the other hand , as the metal ions diffuse downward , gels with capillary structures are obtained and the method is termed (descending technique).[15,16,32]

As is shown by Thiele and Coworkers[19] when the metal ion diffuse upward into the polyelectrolyte solution (ascending technique) , five successive structural zones are formed as shown below:



1) Membrane zone.

2) Dropwise exfoliation zone.

3) Zone of capillaries.

4) Zone of lenses.

5) Zone of stripes.

Gels mostly of capillary structures obtained by downward diffusion may serve as models of a number of biological tissues such as skin , lens , aorta and so on . Thiele et al .[15,16] have investigated in details the processes of formation of capillary gels and their structures . The conditions of formation of zones of lenses and the stripes and their structures have been studied by Tostoguzov. [33,34] His microscopic investigations showed that the transverse sections of calcium alginate are consisting of lenses and stripes . Such lenses and stripes are not found along the whole length of the gel specimens , but they appear at a distance (1~3mm)from the diffusion boundary . The initial zone of gel (1~3mm) is of capillary nature in harmony agreement with that observed by Thiele and Coworkers. [16] The length of the gel zone with transverse drawings was found to be (7~9 mm) . The final

zone which represents to the macroscopically homogeneous gel was found to be about (5~6mm). The presence and absence of strips and lenses is dependent on several factors.

1)Size of cuvette.

2)Initial concentration of alginate sol.

3)Direction of metal ion diffusion flux with respect to gravitional field.

It has been established that the gels with a distinct "stripped " structure are formed only in cuvettes with no more than (2.2mm) in diameter (thickness) and at the initial sodium alginate concentration 1~2.5 wt%. As the magnitudes of cuvette diameters and the initial concentration of alginate deviated from those mentioned above , an ever-increasing deformation of bands took place .

The gel formation by the process of direct diffusion in polyelectrolyte solution is of great importance from the stand point of physical and colloidal chemistry as well as the biological view.

In view of all the foregoing aspects , the present investigations have been undertaken in order to throw some light on the chemistry of polysaccharides in particularly metal-alginate gel complexes in terms of the physical properties and morphology.

II . 2.Experimental

II- 2 . Experimental :

II-2.1.Materials:-

Sodium alginate used was Cica – Reagent (Kanto Chem Co .) .All other materials used were of from (BDH) . And were used without further purification.

Water-soluble metal-salts for Zn(II) , Cd(II), Sn(II), Hg(II) and Pb(II) in the forms of nitrate or chlorides were used in the preparation of electrolyte solutions.

Distilled water was redistilled from alkaline permanganate and degassed by pubbling nitrogen through it , boiling , and cooling under nitrogen atmosphere. [35]

II-2.2.Preparation of Sodium Alginate Sol:-

Sodium alginate sols of different concentration ranging from one to three percent were prepared by dissolving the requisite amount of the solid material in biditilled water. This process was performed by stepwise addition of the powder alginate whilst rapidly stirring the water . Otherwise it gives a lumpy solution which swells with difficulty . The stirring was made at intervals and gently to avoid the breaking of the macromolecular chains , until a clear solution was obtained. The solution was either centrifuged or kept for 24h in order to become air bubble-free.[18,36]

Since the viscosity of sodium alginate increases with increasing the sol concentration , it is difficult to obtain sols of concentration higher than five percent . The latter was very viscous so that it could not flow and was unstirrable.

a - Storage:-

The sols prepared have to be kept in a refrigerator adjusted to about 5°C to prevent the bacterial attack. Thus caused shortening of the chain length which

could be proved by occurrence of a sharp decrease in viscosity. The alginate sols are useful within couple of weeks .

b -Viscosity- Measurements of Sodium Alginate Sols :-

Measurements of solution viscosities are usually done by comparing the efflux time t required for a special volume of polymer solution to follow through a capillary tube with the corresponding efflux time t_o for a solvent (usually water) . From t and t_o and the solute concentration , several quantities are derived .

The viscosity is usually measured in capillary viscometers of Ostwald-Fenske or Ubbelohde type. In the present work, the first one was used in measurements as described elsewhere. [37]

The viscosity measurements were made in a constant temperature water-bath regulated to at least ± 0.05°C. The efflux time was kept long to minimize the need for appling corrections to the observed data . The viscosities were calculated from the following relationships,

Relative viscosity $\eta_{rel} = \dfrac{\eta}{\eta_o} \simeq t / t_o$

Specific viscosity $\eta_{sp} = \dfrac{\eta - \eta_o}{\eta_o} \simeq \dfrac{t_1 - t_o}{t_o}$

Reduced viscosity $\eta_{red} = \eta_{sp} / C$ dl/g

Inherent viscosity $\eta_{inh} = (\ln \eta_r) / C$ dl/g

Where η is the viscosity of the solution ,η_o is the viscosity of the pure solvent and C is the alginate concentration (wt/wt) . The results are summarized in Table II.2. 1 .

II-2.3.Preparation of Electrolyte Solutions :-

Stock solutions (1.0M) of metal ion electrolytes were prepared by dissolving the requisite amounts of the corresponding water-soluble salt in bidistilled water.

The concentration of these stock solutions were determined complexometrically as reported elsewhere. [38]

II-2.4 . Preparation of Cross - Linked Metal Alginate Ionotropic Gel Complexes :-

Ionotropic cross-linked metal alginate gel complexes were prepared by the replacement of Na^{+} counter ions of alginate macromolecule by the corresponding polyvalent metal ion . The shape of the metal alginate prepared depends on the direction of diffusion and the apparatus used.

a.Gel-Membranes:-

This type of gel membrane was achieved using Petri-dishes of 10 cm diameter and 2.5 cm height . These Petri-dishes were smeared with a very thin layer of alginate sol used and dried in a electric oven at 105~110°C for about 30 min. Then it cooled, and was filled with the alginate sol used to about two-thirds of its height and was carefully immersed in 1M of the corresponding metal electrolyte solution . A primary membrane is formed on the surface of alginate sol and grows to a certain thickness (1cm in six hours and 2cm in 10 hours , for 1% and 2% alginate sols , respectively). The formed membrane is carefully removed from the petri - dish walls and washed frequently with deionized water until the resultant

water was free from metal ion (qualitative test) . Then , the membrane is kept in deionized water

b . Gel –Droplets :-

In this case , droplets of sodium alginate of known concentration were allowed to fall from a glass - syringe into a container containing the corresponding metal ion electrolyte solution of known concentration . The droplets will flow on the surface of electrolyte for a period of time depending on the nature and concentration of metal ion , the concentration of alginate sol and temperature . After this time interval is elapsed , the droplets start to sink into the electrolyte solution which means an exchange completion between the Na^+ counter ions of alginate sol in the droplets and the metal ions of the electrolyte solution . These droplets were collected and washed several times as before until the resultant water was free from the metal ion (qualitative test). Then , the droplets are kept in deionized water .

C .Gel- Columns:-

Microstructure of such gels depends mainly on the direction of diffusion .

i-Gels with non-capillary structure:

In this method , open columns of 15 cm height and 5cm in diameter was covered from one side by cellophane membrane . This column was previously smeared with a very thin layer of alginate sol used and dried in an electric oven at 105-110°C for about 30 minutes , then cooled at the room temperature . Hence , it filled with alginate sol to about one-thirds of its height and partially immersed in 1M of the corresponding metal ion electrolyte. The thickness of growth depends on

the concentration of alginate sol (1 cm height in 24 hr for 1% alginate sol) . Hence , the gel formed is carefully removed and treated as previously described .

ii-Gels with capillary structure:-

In this method the metal ion electrolyte is poured on the internal walls of the previously treated column containing the alginate sol to avoid deterioration of the primary membrane formed on the immediate contact of the electrolyte with the sol surface (in this case no need to use cellophane paper and tubes of one – side closed are used) .

d . Gel-Granules :-

Moreover , ionotropic cross-linked metal alginate gels can be obtained in the form of granules . This process is performed by stepwise addition of alginate salt to metal ion electrolyte solution in excess (about 1.0M) while rapidly stirring the solution to avoid the formation of gelatinous precipitate which swells with difficulty. After completion of exchange , the metal alginate granules formed were washed with deionized water , followed by doubly distilled water until the washings became free of the metal ions . The gel sample was dried at 100°C under vacuum over anhydrous $CaCl_2$ or P_2O_5 and kept in disccator until it be used.

II-2.5-Physical Properties Measurements :-

a-Water-content (%) :

A fixed number of spherically pellets for different polyvalent metal ions were gently dried with filter papers several times . Then weighted and placed in an

electric oven at 120 °C until constant weight reached . The water content was calculated from the relationship

$$\% = \frac{W_o - W}{W_o} \times 100$$

where W_o is the initial weight and W is the weight after drying . The results are listed in Table II. 2.2.

b-Droplet Size (V) :-

The size of the droplet was evaluated by the displacement-volume method . A fixed number of pellets were dried as described previously in (a) . Then , the pellets were poured in a measuring cylinder containing a known volume of water . The displacement volume of water is recorded . The size can be given using the following equation :

$$V = \frac{V_1 - V_2}{n}$$

where V denotes the droplet size , V_1 is the initial volume of water and V_2 is the final volume of water in the measuring cylinder . The results are cited in TableII.2. 2.

C-Droplet Radius (r):-

The radius of the droplet can be evaluated from the following relationship:

$$r = \sqrt[3]{\frac{3m}{4\rho\pi}}$$

where m is the droplet mass and ρ is the density of the droplet ($\rho = m / v$) . The results are given in TableII.2. 2.

II-2.6-Elemental Analysis :-

Elemental analyses for C and H for these metal alginate gels were carried out using a Perkin-Elmer 240 °C instrument . The results are summarized in Table II.2.3 .

II-2.7.X-Ray Diffraction :-

The X-ray diffraction patterns were obtained using a Philips 1710 diffractometer with copper target and nickel as a filter (λ=1.54178A°) at 40 kV and 30 mA . The scanning speed was 3.6 min $^{-1}$ in the range of 2 θ = 2~60° (298k) . The diagrams are shown in FigureII.2. 1.

II-2.8-Fourier Transformer Infrared Investigation (FTIR) :

FTIR spectra of metal alginate gel complexes of the grain forms were scanned on a Pye –Unicom SP^3 100 spectrophotometer using the KBr disc technique (4000~200 cm $^{-1}$).

The FTIR spectra of the samples studied are given in Figures II.2.(2~7) . The vibrational assignments of the bands are summarized in Table II.2.4 .

II-2.9- Morphology: -

a-Optical Microscopical Investigations :-

Transverse and longitudinal sections were made in membrane gels prepared by the descending techniques and investigated using an optical microscope . The optical photographs are shown in FiguresII.2.(8~10) . Again a microscopical scanning in the structural pores are also presented .

b-Electronmicroscopical Scanning :-

Samples for electronmicroscope investigation were furnished . The preparation of these samples was performed by taking micro small pieces of the membranes previously prepared (p. 47) and dehydrated using 30,50,70 and 95% of alcohol for about 30 min in each . Then , the samples were immersed in absolute alcohol for about 30 min , followed by immersing in a 1:1 mixture of absolute alcohol and methaacrylate and finally in pure methaacrylate for the same time . One piece was then placed in a capsule of gelatin containing a mixture of methaacrylate and 1% benzyl peroxide (as accelerator) . The capsules were then placed in an oven for 24 hrs at 60 °C .

The metal alginate in the capsules was sliced by an ultramicrotom , then collected on grids to be ready for photographing . The SEM photos are shown in FiguresII.2.(11~15).

II.3.Results and Discussion

II.3.Results and Discussion :

The usefulness of solution viscosity as a measure of polymer molecular weight has been recognized a long time ago . Solution viscosity is basically a measure of the size or extension in the polymer molecules . It is empirically related to molecular weight for linear polymer such as sodium alginate .[39]

The viscosity of sodium alginate plays a very important role in the physical properties of the gel formed which depends on the pH and the source of alginate . It defined as the force per unit area required to maintain a unit velocity gradient between two parallel plates kept a constant distance apart or the definite energy transformed into heat per unit of time and per unit volume of liquid .

The viscosities of sodium alginate sols at various concentrations and temperatures are summarized in TableII.2.1. The data obtained indicated the increase in viscosity values with increasing the concentration of alginate sol , whereas a decrease in the viscosity was observed on increasing the temperature.

Metal alginates in form of pellets showed good mechanical properties . They are symmetrically spherical , elastic and having good transparency than other alginate gels . The water content , weight , volume , size, elasticity and transparency of these pellets are listed in Table II.2.2 . This result indicated that the water content exceeds 90% for all gel complexes studied . The elasticity follows the order Pb > Cd > Zn > Hg ≃ Sn. Again , the radius increases in the following order.Pb < Zn < Cd < Hg < Sn .

The mechanical properties play a very important role in the exchange processes and can be considered as a determining factor for the mechanical stability of the gel complex .

The elemental analyses for these metal alginate complexes are cited in TableII.2. 3 . The good agreement between the experimental and calculated values may confirm the reproducibility of the results obtained. The number of coordinated water molecules cited in TableII.2. 3 . Were determined from the thermolysis measurements for these gel complexes.

The X- ray diffraction patterns showed in FigureII.2.1 indicated that all metal alginate gel complexes studied are amorphous in nature . This result is in good consistent with that obtained for another metal alginate complexes which reported earlier. [40,41]

The infrared spectra of the metal- alginate complexes were measured . The vibrational assignments of the bands are given in TableII.2. 4 . The band of sodium alginate at 1600 (υ_{as}) and 1400 (υ_{s}) cm^{-1} correspond to the stretching vibrations of the(- OCO-) group while the band at 3500 cm^{-1} belongs to the stretching vibration of the hydrogen bond of the hydroxyl group. [42]

The bands of the complexes indicate that the band at 1600 cm^{-1} is shifted to 1601- 1655 cm^{-1} whereas the band at 1400 cm^{-1} is shifted to 1403-1421 cm^{-1} as shown in FiguresII.2.(2-7). This indicates the participitation of these groups in the coordination . The shift in the υ OH band to the lower frequency is quite large for all metal chelates as indicated in Table II.2. 4 and it becomes less broad then that of sodium alginate Figures II.2. (2-7) . Thus both (-OCO-) and (- OH) groups take part in the coordination for all the metal alginate complexes studied .

Again the free ligand has a strong band located at 1735 cm^{-1} which can be assigned to the carbonyl stretching vibration of the carbonyl group. [31] The displacement of this band to higher frequencies in the spectra may confirm the

coordination of the carboxylate group . The location of υ_{as} OCO is diagnostic of abridging carboxylate group .

The morphology of gels has received considerable attention . However , the role of solvation in their structure does not always permit them to be maintained unchanged on application of special methods of investigations such as electron-microscope preparation techniques . Thus , it may be impossible to obtain picture of unchanged gel systems .

The present investigation aims not only to maintain the original gel structure but to prepare gels having ordered structures by sol-gel transformation .

The diffusion of Zn (II) , Cd(II) , Sn(II) , Hg (II) and Pb(II) ions into the alginate anionic polyelectrolyte results in ionotropic formation of ordered gels . These gels show birefringence , swelling anisotropy , ion exchange capabibility , and under certain conditions capillary structure (downward diffusion) . The formation of these structures is a result of a complicated sequence of steps .

Optical images for transverce-and longitudinal sections are shown in FiguresII.2. (8-10) . These gels show uniform capillaries perpendicular to the ion front in the longitudinal view , whereas pores of the same diameter are obtained in the cross-section photos .

This structure regularity of gels is always observed when a certain counterions diffuse into polyelectrolyte as has been demonstrated with various systems of polyelectrolytes. [18,43-50]

Mechanism of Sol-Gel Transformation: -

An explanation of the ordered gel formation can be based on the random distribution of the macromolecules of alginate in the dispersion medium . In this case of maximum entropy , the sol containing anisometric particles is isotropic .

Ionotropy is the orientation of anisotropic sol particles by ions in such a away that coagulation and the formation of anisotropic gels are effected . When an electrolyte solution of a polyvalent metal ion such as in the present study is carefully brought into contact with alginate sol polyanion , counterions of the electrolyte solution slowly diffuse into the alginate sol . The diffusing counterions are attracted to the oppositely charged sites on the polyelectrolyte molecules , thereby reducing the charge density of the latter and diminishing their tendency to hydrate . This leads to the formation of a thin skin primary membrane (pellicle) at the interface between the alginate sol and the metal ion electrolyte . This primary membrane prevents the colloidal polyelectrolyte from diffusing into the electrolyte solution (and allows the cations of both the alginate sol and electrolyte solution to diffuse in the reverse direction) . Hence , the macromolecular chains of the alginate polyelectrolyte start to distribute themselves statistically downside the formed membrane. As a steady state approached , the metal ions of the electrolyte begin to diffuse through the already formed membrane inside the alginate sol . Simultaneously , the counter ions resulting from the dissociation of the sol , Na + , start to diffuse through the membrane outside into the electrolyte . A diffusion potential will be established [51,52] owing to the different mobilities of the exchanging ions . The electric field resulting from the diffusion potential causes uncoiling , flattening and orientation of the charged alginate macromolecules parallel to the ion front and membrane . The result is a net dehydration of the sol

followed by gelation . This process repeats itself with the newly formed pellicle so that the gelation zone penetrates into the sol , resulting in the formation of capillaries Figurs II.2 (8~10). Therefore , a cohesive gel is formed from many individual membrance.

The structure of ionotropic gel membranes depends on the type and concentration of the counterions , pH of the electrolyte solution; type, concentration , anisotropy , chain length of polyelectrolyte , viscosity and temperature.

Electronmicroscopy and scanning electronmicroscopy [50,53,54] have provided the physical basis for understanding the causal relationships between cellular structure and resistance to material transport , facilitating the tailor-making of physical gel structures, correlating of gel structures with vibrations in fabrication procedures as well as furnishing more detailed and unequivocal pore statistics . Electron microscopic photomicrographs are presented in FiguresII.2.(11 ~15) .

This electron microscope investigations reveal that the capillary gel is in the plane at the origin of capillary growth . Here , the capillaries are uniform in diameters and are regularly distributed over the plane . Its also reveal the orientation and the tangential arrangement of the coherent net work in the walls of capillaries.

The formation of the capillary structure in these orderd gels starts with the creation of a membrane at the interface of electrolyte and the sol , which due to a partial dehydration (shrinking). The contraction of the membrane cause an increase in the content of solid matter , the water from the dehydration segregating as small droplets within the meshes of the network in the gel . This result in phase separation by demixing . The demixing process by segregation of droplet will be

the slower and depends essentially on the nature of electrolyte penetrating into the sol .

In places the droplets can unite to form bigger drops . In the growing gel , the drops are pushed onward by the diffusion front , and their paths give rise to the capillary structure of the gel . At the sol-gel interface , the water drops do not mix with the sol . Here , in our experiments the linear molecules undergo orientation perpendicular to the ion flow . As the capillaries reaching up to the gel zone act as radial diffusion centers , the linear macromolecules are additionally ordered tangentially to the capillaries in the plane of the system perpendicular to the ion flow .

The net result of investigations of the formation of ordered gel with Na-alginate suggest that gel formation by ion diffusion in polyelectrolyte system is a general principle of structure formation . This process is colloid chemical process . Again , the electronmicroscopic investigations provide information of the morphology of capillaries in these gels and reveal the orientation and the tangential arrangement of the coherent spatial network in the walls of capillaries . It reveals the presence of one or two extreme types of structural formations , reticular and compact structures , respectively as observed with other gels earlier. [50,55]

Table II.2 . 1 : The relative , specific , reduced , inherent and intrinsic viscosities as functions of temperature and sodium alginate concentration .

Alginate ,%	1 %				2 %			
Temp.,°C	η_{rel}	η_{sp}	η_{red} dl / g	η_{inh} dl /g	η_{rel}	η_{sp}	η_{red} dl / g	η_{inh} dl / g
25	55	54	54	4.01	150	149	75	4.32
35	48	47	47	3.89	116	114	57	4.06
45	42	41	41	3.73	95	94	47	3.86
55	37	35	35	3.61	81	80	40	3.70

Table II.2 .2:The water content , size and radius for metal alginate ion-otropic gel complexes in the pellets form .

[Alg] =2 % and Temp . = 35°C

Physical property / Complex	Water content%	Weight 10^{3} g	Size 10^{2} cm^{3}	Radius 10^{2}cm	Elasticity	Transparency
Zn(II) - alginate	94.87	19.05	1.50	15.33	elastic	transparence
Cd(II)-alginate	95.91	22.05	1.63	15.87	elastic	transparence
Sn(II) –alginate	90.01	36.97	3.00	19.50	elastic	transparence
Hg(II)- alginate	90.51	29.55	2.13	17.28	elastic	transparence
Pb (II)-alginate	95.03	20.13	1.38	15.01	elastic	transparence

Table II.2. 3: Analytical data for metal alginate ionotropic gel complexes .

Complex	Found (%)			Calculated (%)			Formula
	C	H	M	C	H	M	
Zn(II)-alginate	31.52	4.23	14.33	31.76	4.41	14.41	$C_{12}H_{14}O_{11}Zn.3H_2O$
Cd(II)-alginate	28.54	3.75	22.31	28.78	3.99	22.46	$C_{12}H_{14}O_{11}Cd.3H_2O$
Sn(II)-alginate	29.41	3.52	24.24	29.45	3.68	24.32	$C_{12}H_{14}O_{11}Sn.2H_2O$
Hg(II)-alginate	25.01	3.08	35.01	25.23	3.15	35.13	$C_{12}H_{14}O_{11}Hg.2H_2O$
Pb(II)-alginate	24.73	3.09	35.72	24.95	3.12	35.90	$C_{12}H_{14}O_{11}Pb.2H_2O$

Table II.2 . 4:Infrared frequencies (cm^{-1}) for sodium and metal alginate ionotropic gel complexes .

Compound	υ_s OCO	υ_{as} OCO	υ OH	υ M-O
Na –alginate	1400	1600	3500	850
Zn (II)-alginate	1421	1655	3477	821
Cd(II)-alginate	1418	1601	3489	820
Sn(II)-alginate	1403	1636	3421	813
Hg(II)-alginate	1405	1620	3461	816
Pb(II)-alginate	1407	1631	3448	815

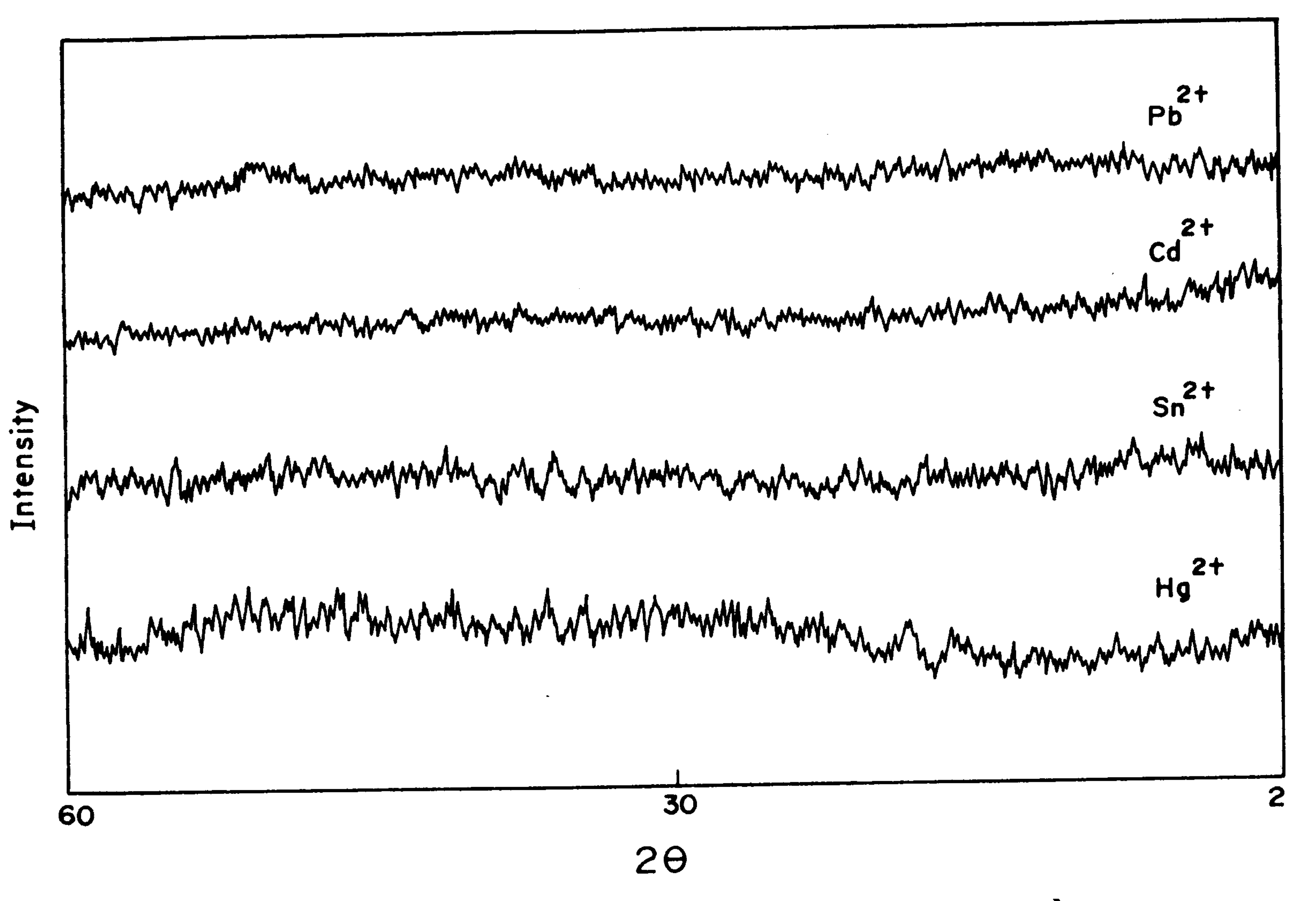


Figure.II.2.1: X– ray diffraction patterns for some metal - alginate gel complexes (298 k) .

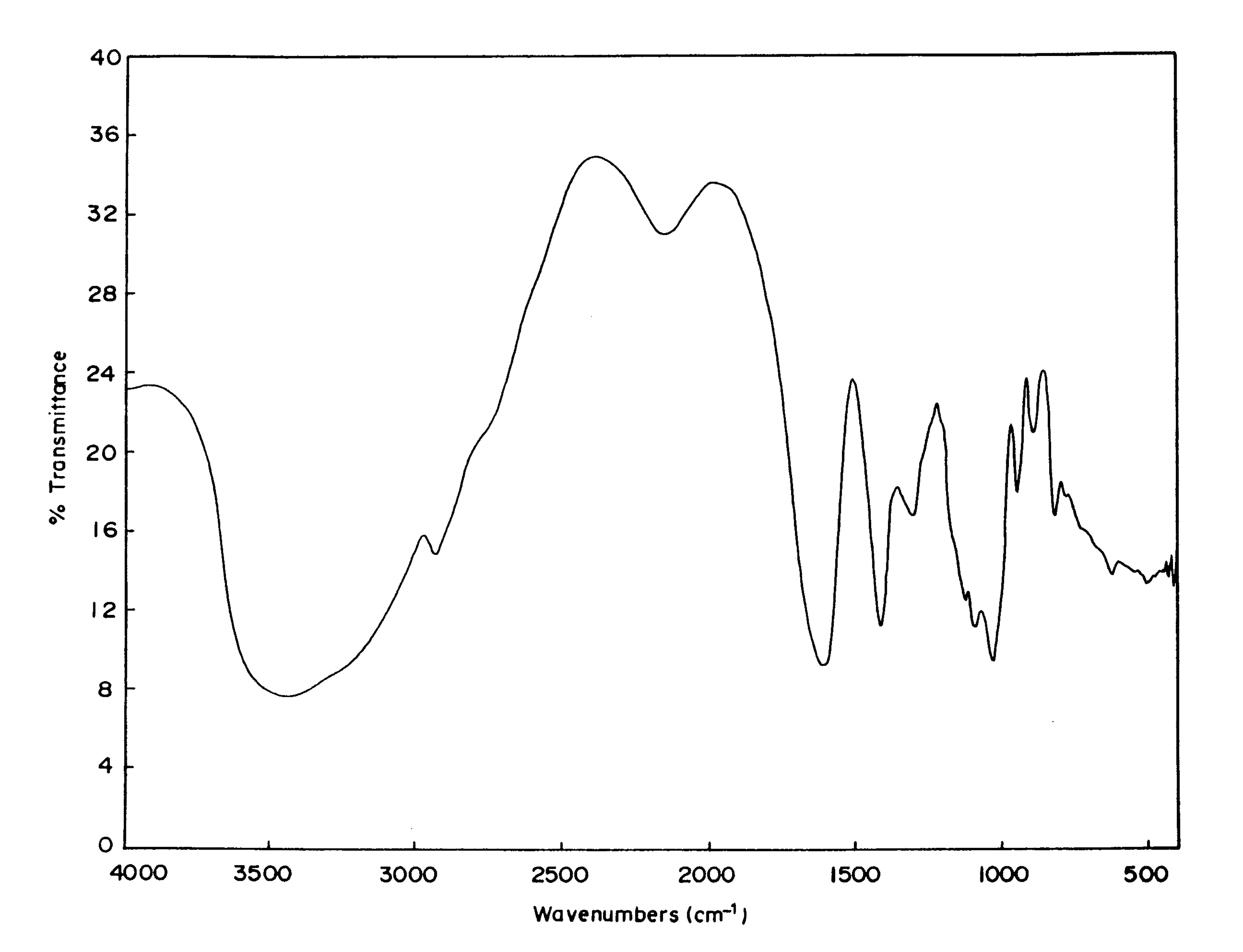


Figure . II.2.2: Infrared spectra for alginate macromolecule.

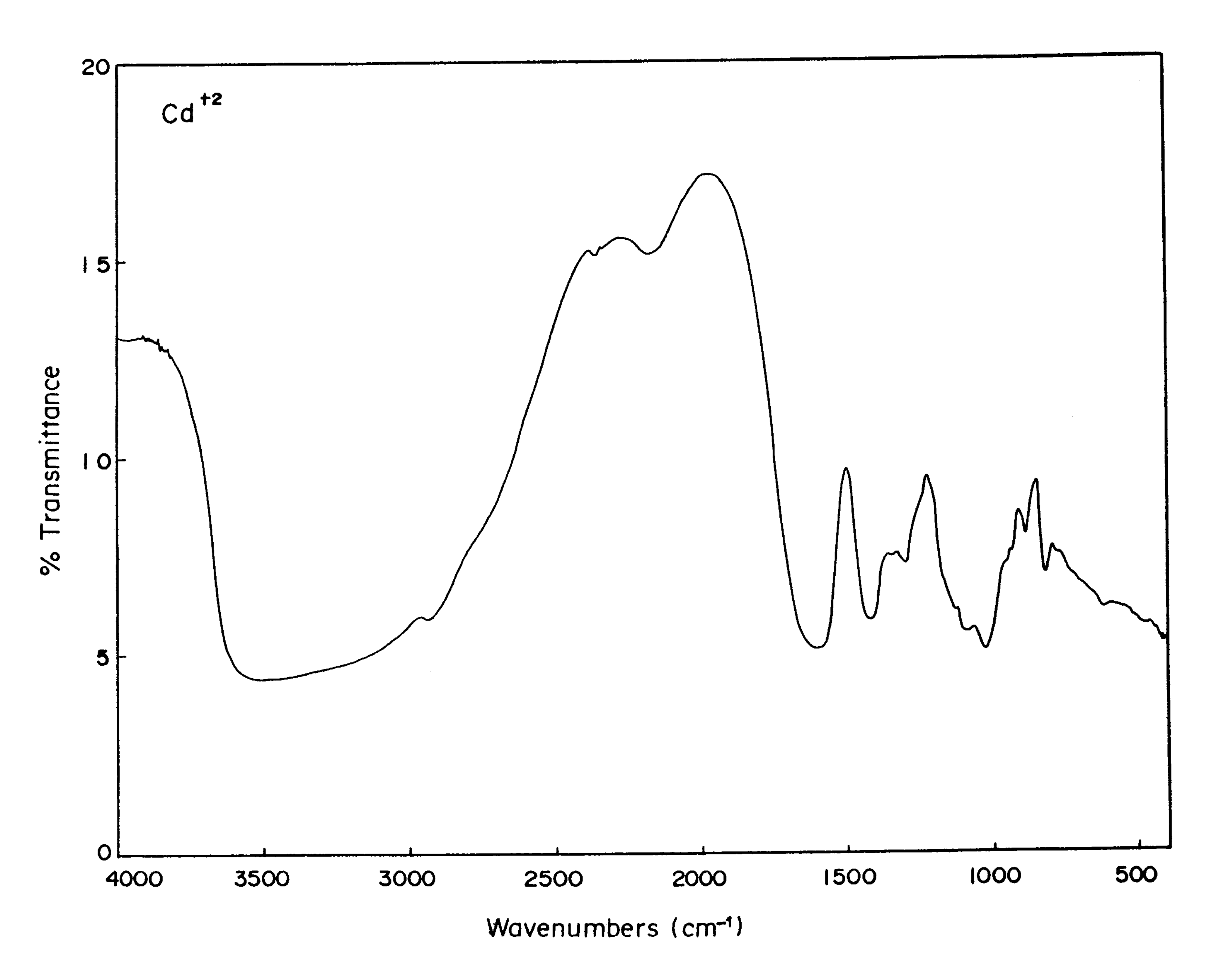


Figure . II.2.3: Infrared spectra for Cadmium (II)- metal alginate gel complex .

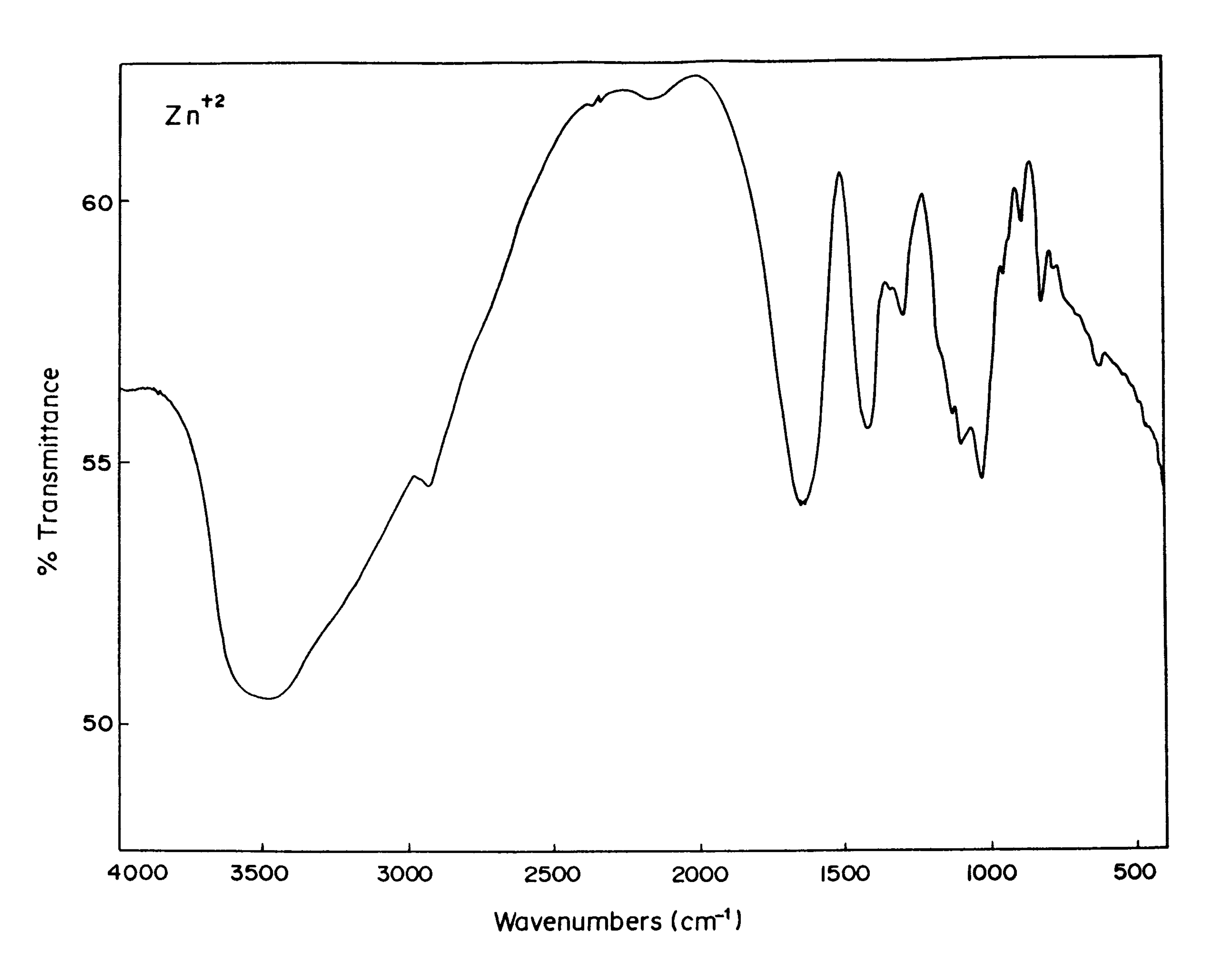


Figure .II.2.4: Infrared spectra for Zinc (II) –metal alginate gel complex

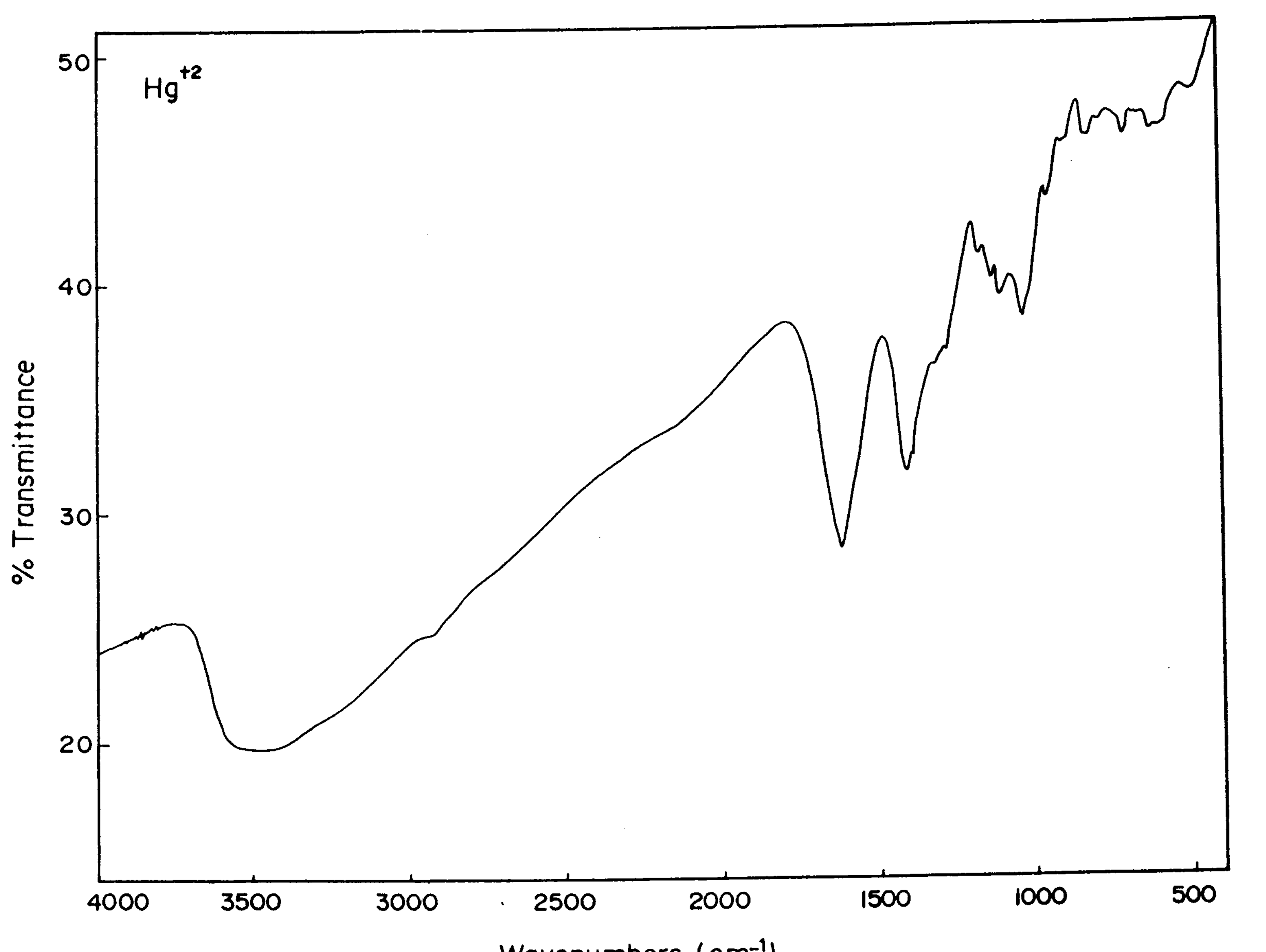


Figure . II.2.5: Infrared spectra for Mercury (II)-metal alginate gel complex .

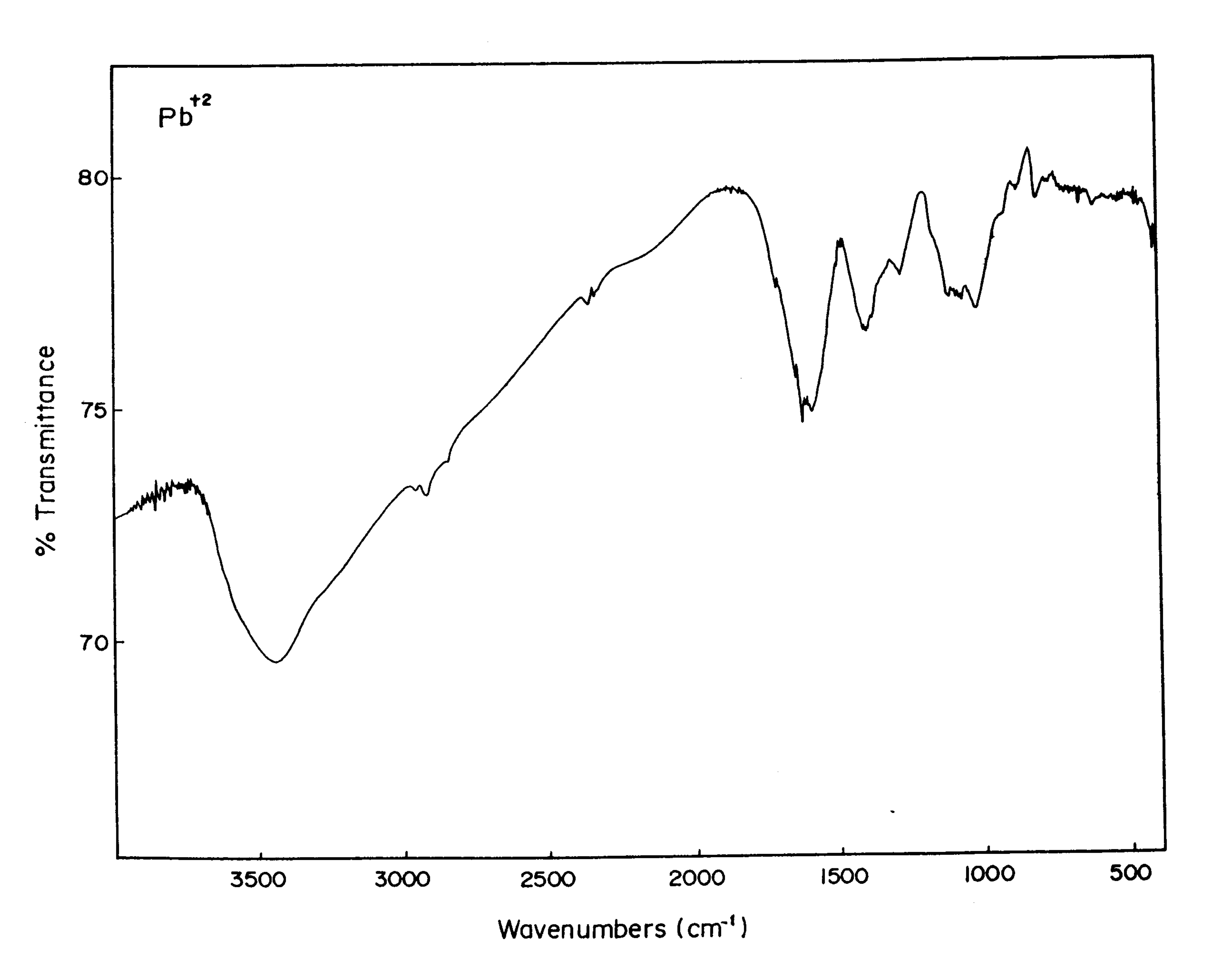


Figure. II.2.6: Infrared spectra for Lead (II)–metal alginate gel complex.

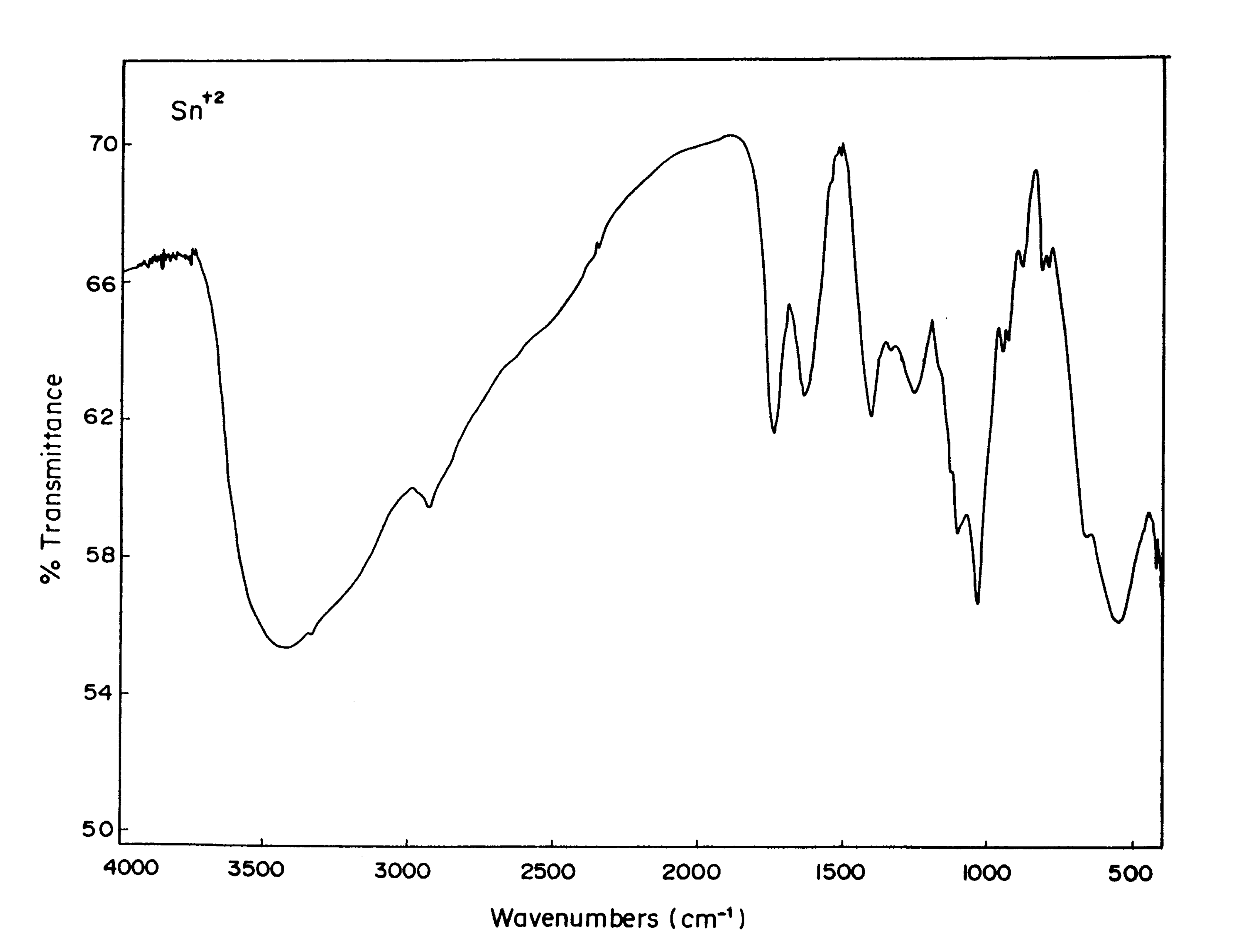


Figure.II.2.7: Infrared spectra for tin (II) - metal alginate gel complex .

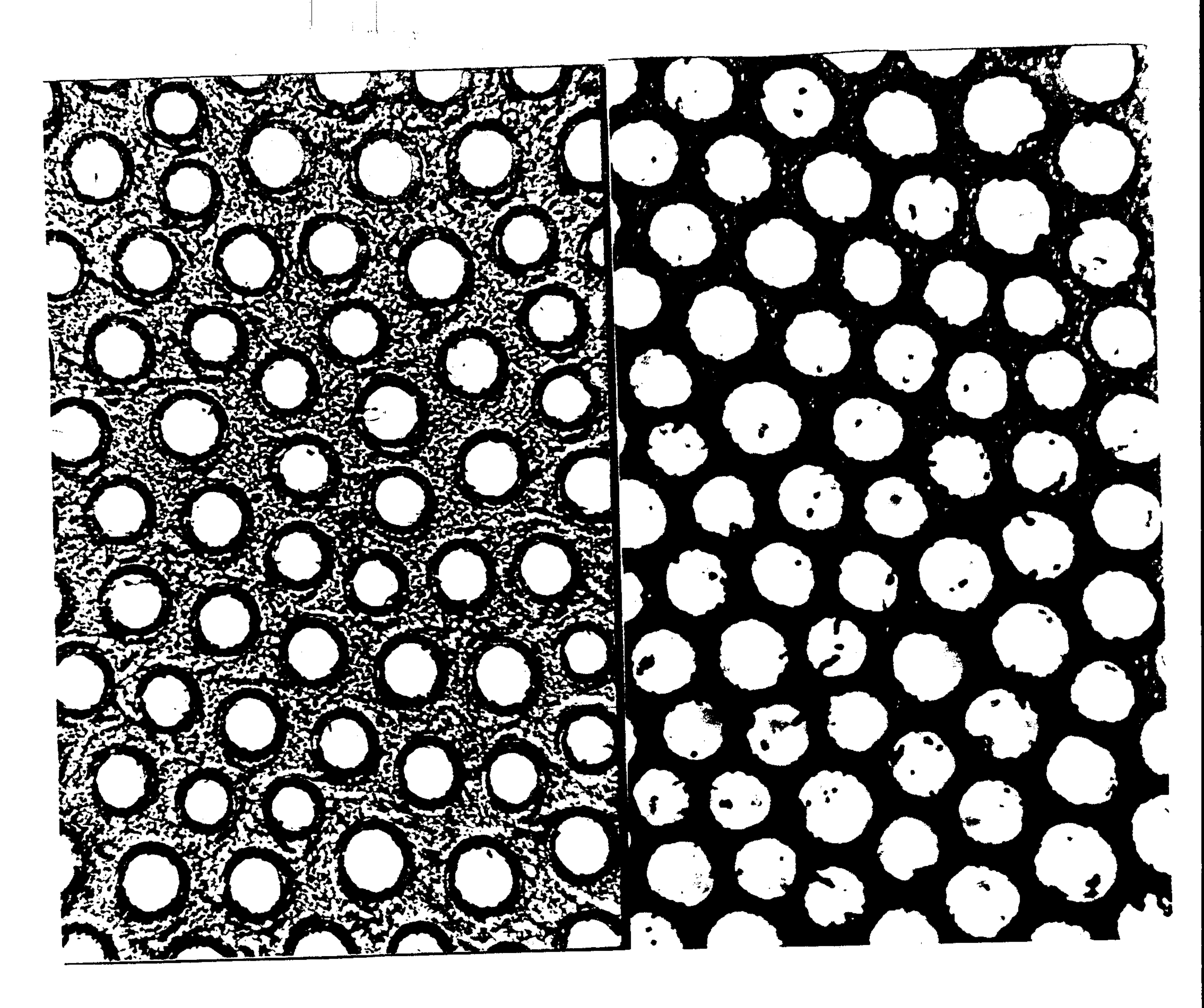
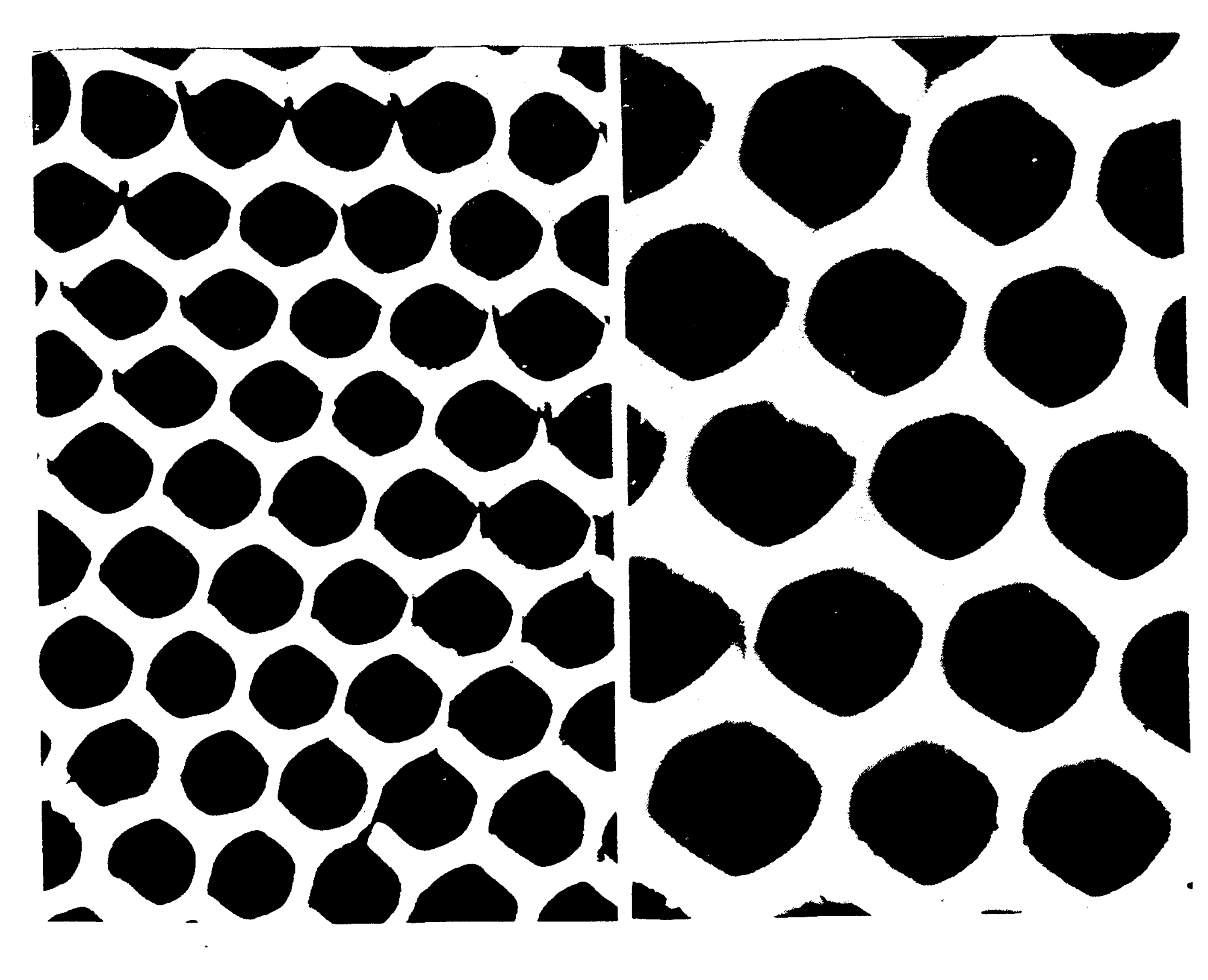


Figure II.2.8.Optical images of transverce sections in ionotropic metal alginate gels .



Pb^{2+} Hg^{2+}

Figure-II.2.9.Optical images of transverce sections in ionotropic metal alginate gels .



Cd^{2+}

Figure II.2.10.Optical image of longitudinal sections for metal alginate gels .

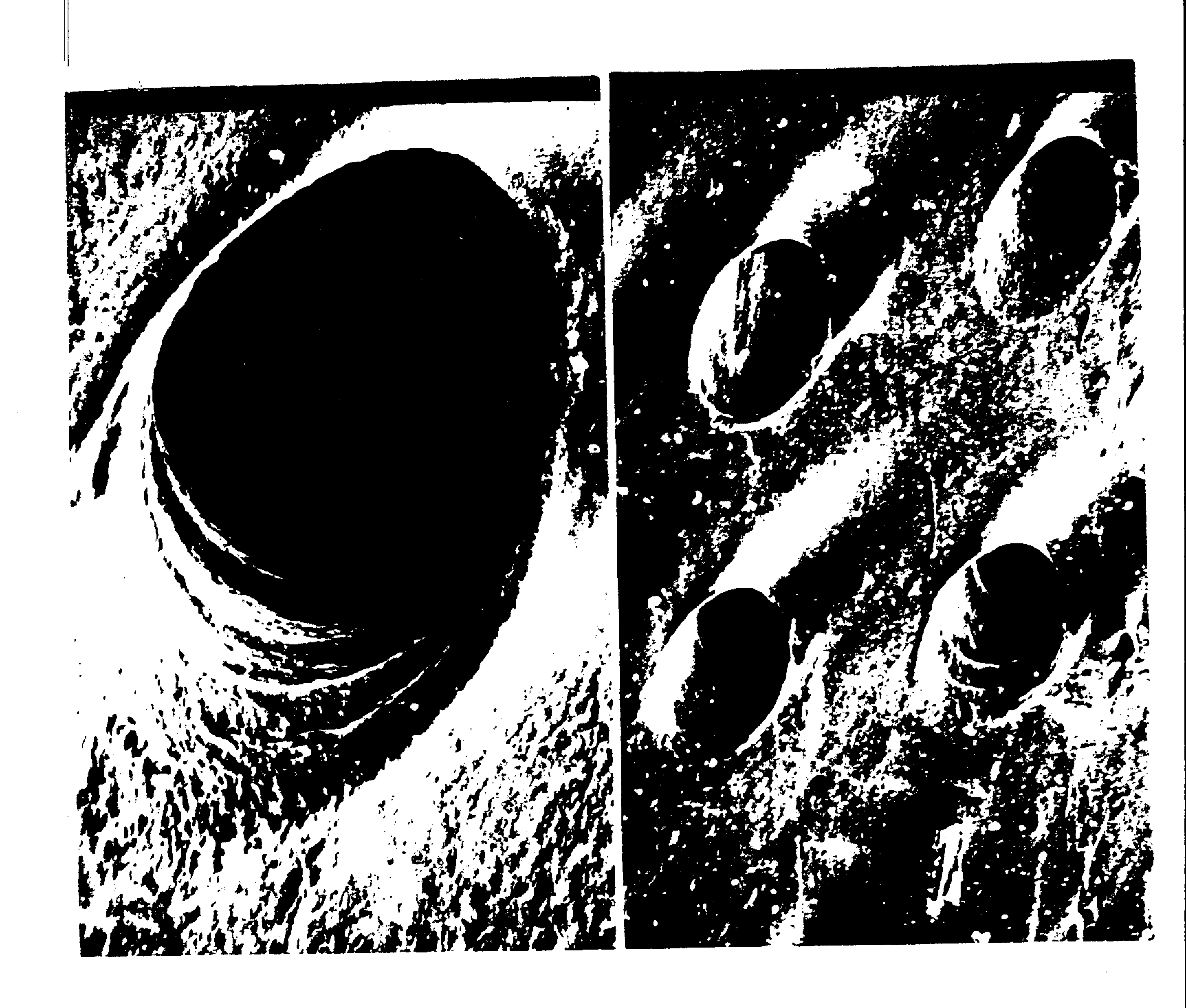


Figure II.2.11. Scanning electron micrographs of the inside the pores of ionotropic metal alginate gels .

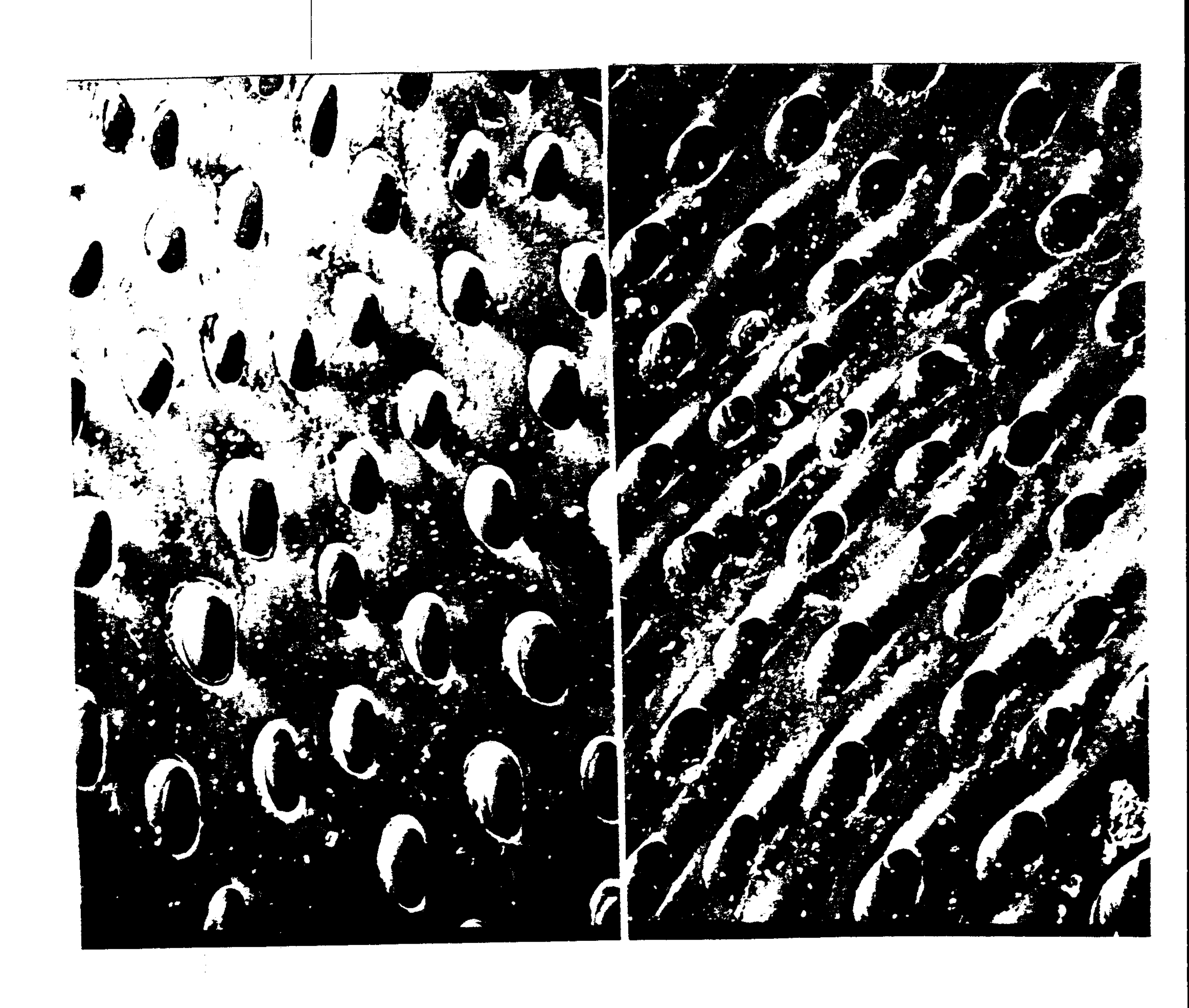
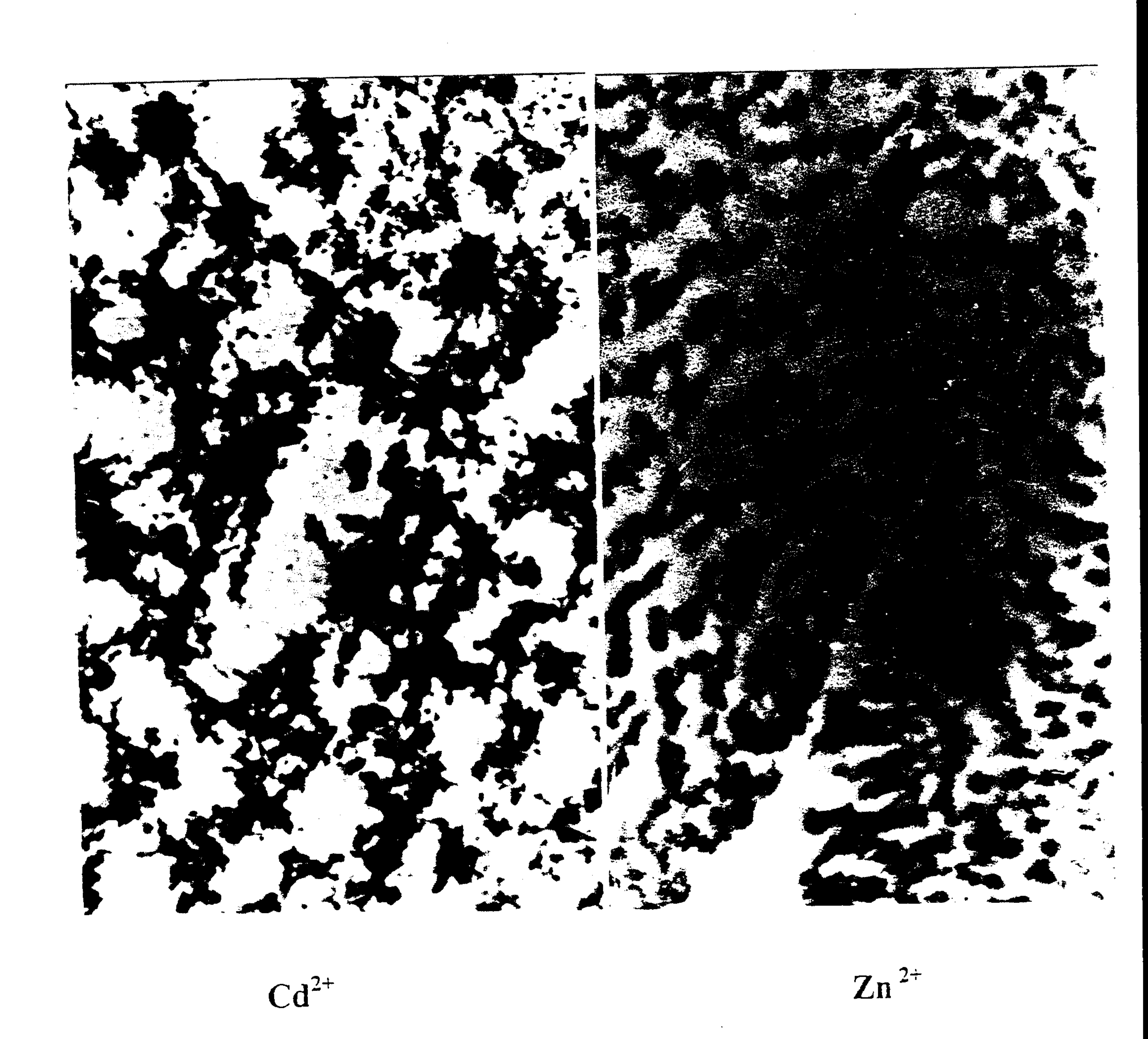
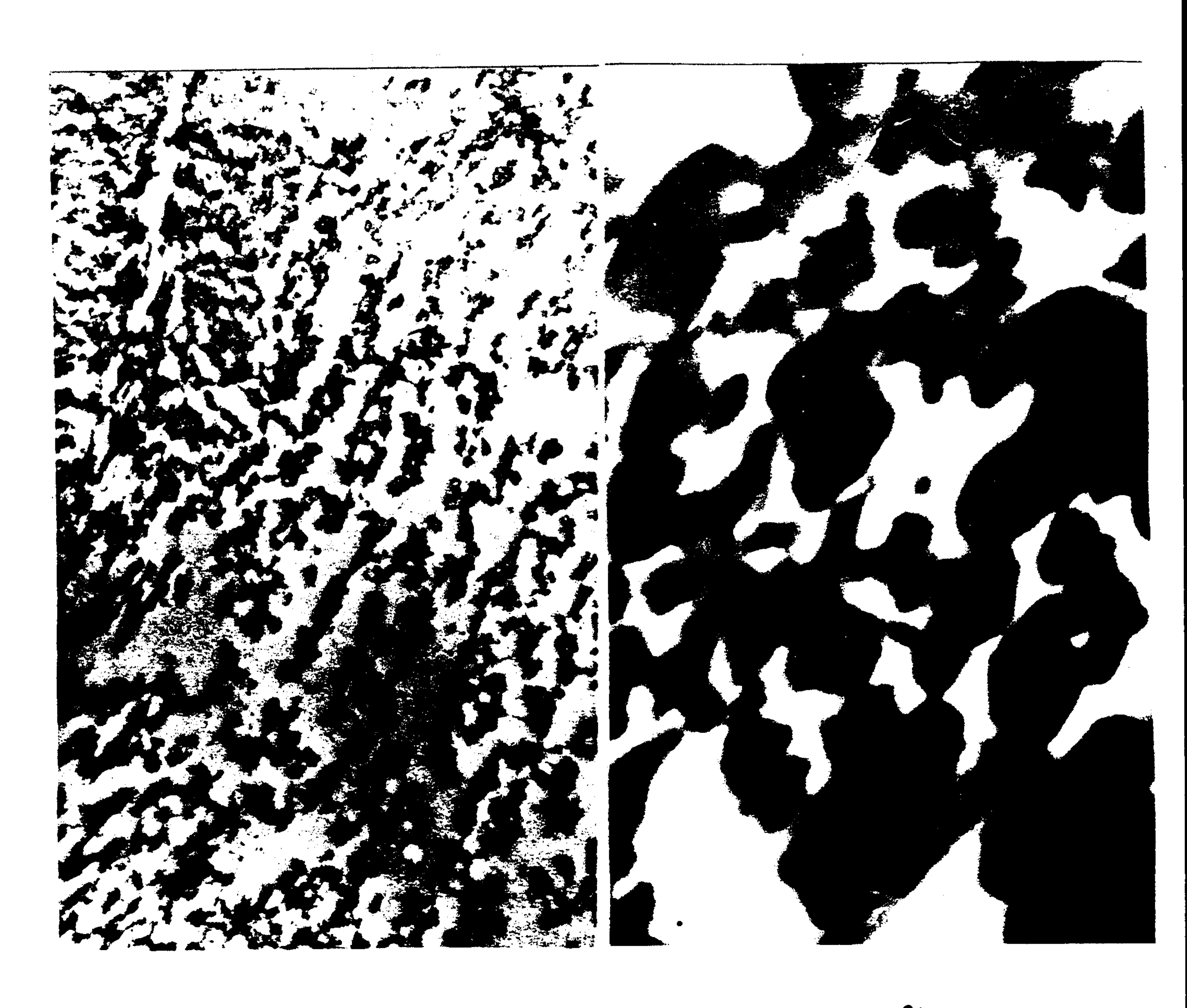


Figure II.2.12. Scanning electron micrographs of the inside the pores of ionotropic metal alginate gels .



FigureII.2.13. Scanning electron micrographs of ionotropic metal alginate gels .



FigureII.2.14. Scanning electron micrographs of ionotropic metal alginate gels .



Hg^{2+}

Figure II.2.15. Scanning electron micrographs of ionotropic metal alginate gels .

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CHAPTER III

Influence of Diffusion Controls On Relaxation Time and Velocity of Acceleration For Metal Alginate Ionotropic Gel Complexes

III . 1. Introduction

III.1.Introduction :

Sodium alginate has a high affinity to chelate with polyvalent metal ions in an egg-carton like structure. (1~3) This chelation takes place through the replacement of Na^+ counterions of alginate macromolecule by the corresponding polyvalent metal ions . A such exchange process leads to the transition of the alginate sol into the gel form as follows:

$$Z(Alg-Na)_n + M^{Z+} = (Alg_Z - M)_n + Z\,Na^+ \qquad (1)$$

sol electrolyte gel electrolyte

The chelation is not such simple where a sort of bridge , between the metal ions and both the carboxylate and hydroxyl functional groups of alginate chains, is formed . The sol – gel transformation occurs stoichiometrically. (4~6) The rate of gelation depends on many factors such as the nature , density , pH and concentration of the metal ion electrolyte solution as well as the source and concentration of the alginate sol. (7~13)

As an alginate sol droplet gets in contact with a polyvalent metal ion electrolyte , a thin primary membrane is formed around the droplet at the interface between the electrolyte solution and alginate sol . This formed membrane will separate the alginate sol and prevents it from diffusion into the surrounding electrolyte. Simultaneously , an exchange process occurs between the alginate counter ions (Na^+) and the electrolyte metal ions (M^{2+}) in the reverse direction.

At the beginning , the droplet floats just below the surface of the electrolyte for a certain period of time since its density is smaller than that of the electrolyte solution . This time period may be called by the relaxation time ($\Delta\tau$) . Several factors play important roles on the relaxation time . After the relaxation time

interval has elapsed , the metal – alginate droplet starts to sink into the electrolyte solution with an appreciable velocity .

Hassan and Coworkers [14] investigated the influence of diffusion controls, such as the mass , radius , size and density of the droplet as well as the density , viscosity and pH of the electrolyte solution, on the relaxation time and velocity of falling with respect to Mn (II) , Co (II) ,Ni(II) ,Cu (II) and Zn (II) divalent transition metal ion alginate droplets .

Therefore , the present work is of great significant and has been undertaken with a view to shed some light on the gelation process with respect to the heavy metal ions . The results which obtained may explain the mechanistics of the diffusion controls on the relaxation time and , hence , the rate constant of gel growth .

III . 2.Experimental

III.2.Experimental:

Sodium alginate used was Cica – Reagent (Kanto Chem . Co .) . All other materials were of from (BDH)grade . Double distilled deionized water was used in all preparations . The temperature was controlled within ± 0.1 °C .

III.2.1.Preparation of Sodium Alginate Sols :

The preparation of alginate sols and its storage were as described in chapter II (p . 43) .

III.2.2.Preparation of Metal Ion Electrolyte Solutions :

Electrolyte solutions for Cd (II) , Sn (II) , Hg (II) and Pb (II) of various concentrations were prepared and standardized as described in chapter II (p .45) and chapter IV (p .115)

III.2.3.Relaxation Time Measurements:

A droplet of sodium alginate sol of known concentration was allowed to fall from a dropper such as a glass- syringe into a calibrated cylindrical tube of 2 cm width containing metal ion electrolyte solution of known concentration which was previously thermostated into a water – bath at the desired temperature within ± 0 .1 °C . The time of contact of the alginate sol with the electrolyte surface is recorded . Then , the time intervals between the moment at which the droplet gets in contact and the moment at which the droplet starts to sink into the electrolyte solution were measured . This time intervals denote the relaxation time for the gelation process between the alginate sol and the metal ion ($\Delta\tau$) .

For each alginate sol and metal ion electrolyte , some precautions were taken into consideration in order to maintain a nearly constant sol droplet . These precautions are:

1 . Using the same syringe as a dropper .

2 . Keeping the distance from the tip of the syringe to the surface of electrolyte solution fixed .

3 . Using the same volume of alginate sol inside the syringe in order to keep the pressure force on the piston of syringe constant .

III.2.4.Velocity of Acceleration Measurements :

The distance (Y) covered by the droplet while falling into the electrolyte solution was recorded as a function of time (t) . The results are summarized in Table III .3. 1 .

All experiments were repeated with different metal ion electrolyte concentrations at various temperatures unless is noticed . The results obtained were an average of at least five experimental runs .

III.2.5.The Thermodynamic Functions :

Although reactions in the gas phase are simpler to deal with theoretically , the fact remains that most chemistry encountered in practice occurs in solution of one kind or another . Therefore , the kinetics of reactions in the liquid phase can not be interpreted in terms of the kinetic theory and statistical mechanics of gases . The interpretation of rates in solution is necessarily more complicated from a molecular point of view because of the much greater interaction between molecules .

The first question that arises is whether there is any fundamental difference between the kinetics of reaction in solution and in the gaseous state . Briefly , when a reaction occurs by the same mechanism in solution and in the gas , the kinetics are often not changed appreciably . However , because of the increased interactions in condensed media , the mechanism is usually changed completely and the kinetics are greatly altered .

Arrhenius[15] proposed the following empirical equation for calculating the energy of activation of a reaction having the rate constant K at temperature T :

$$K = A\, e^{-E_a/RT} \qquad (2)$$

where : K is the reaction rate

A is the frequency factor

$E^{\neq}_a$ is the activation energy

R is the universal gas constant , and

T is the absolute temperature

The logarithm form will be

$$\log K = \log A - \frac{E^{\neq}_a}{2.303R} \cdot \frac{1}{T} \qquad (3)$$

Hence , plotting log K against $\frac{1}{T}$ should be a straight line from whose slope and intercept, the Arrhenius parameters $E^{\neq}_a$ and A can be calculated , respectively.

According to the theory of absolute reaction rates [16] , the expression for the rate constant of a reaction given by Eyring is

$$K = \frac{k_B T}{h} \; e^{-\Delta G / RT} \qquad (4)$$

where : K is the rate constant

k_B is the Boltzman's constant

h is the planck's constant

$\Delta G^{\neq}$ is the activation free energy

R is the gas constant , and

T is the absolute temperature

Since

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \qquad (5)$$

Substituting Eq . (5) into Eq . (4) , yields

$$-\ln \frac{h}{k_B T} K = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \qquad (6)$$

where $\Delta H^{\neq}$ denotes the enthalpy of activation and $\Delta S^{\neq}$ is the entropy of activation .

Plotting the left hand – side versus $\frac{1}{T}$ should be a straight line from whose slope and intercept the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values can be evaluated .

Another form of Eq (6) may be introduced as follows

$$\log \frac{K}{T} = \log \frac{k_B}{h} - \frac{\Delta H^{\neq}}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S^{\neq}}{2.303R} \qquad (7)$$

also , plotting of log K/T versus 1/T gives a straight line with a slope equals to $\frac{\Delta H^{\neq}}{2.303R}$ and an intercept equals to $\log \frac{k_B}{h} + \frac{\Delta S^{\neq}}{2.303R}$, respectively .

Moreover , a value corresponding to the activation entropy can also be

calculated from Eyring equation knowing $\frac{\Delta H^{\neq}}{T}$ and K at temperature T

as follows:

$$\Delta S^{\neq} = 2.303\ R\ \log\frac{K}{T} + \frac{\Delta H^{\neq}}{T} - 2.303\ R \log \frac{k_B}{h} \qquad (8)$$

III . 3.Results and Discussion

III . 3 . Results and Discussion :

As the alginate sol droplet comes in contact with the electrolyte solution of any metal ion under investigation , a thin film is formed around and the alginate droplet which may be termed by the primary membrane . This membrane prevents the alginate sol from diffusion into the surrounding electrolyte as well as gives the formed droplet a symmetrical spherical shape . Hence , the macromolecular chains of alginate sol start to distribute themselves statically downward along that membrane . When a steady –state condition is established , the sodium counter ions resulting from the dissociation of alginate sol start to migrate outward into the surrounding electrolyte solution . Simultaneously , an equivalent amount of metal cations of the electrolyte solution must migrate inward to occupy the sites left by the sodium ions , eventhough the mobilities and valencies of the two counter ions are quite different. [17, 18] This exchange process leads to the transformation of alginate sol into alginate gel and the process is termed sol – gel transformation .

At the beginning , the density of alginate droplet is smaller than that of the electrolyte solution , therefore , the droplet floats just below the surface of electrolyte . As the exchange process proceeded , a growth in the alginate droplet takes place . This process repeats itself several times leading to the formation of monolayer polymembrane .

The time necessary for the droplet to have surface properties distinctly different from those of the sol , i.e. the droplet density exceeds that of the electrolyte solution can be termed the relaxation time ($\Delta\tau$) . In fact , the relaxation time terminates in very brief periods of time , but for sol – gel transformation the structural peculiarities and the hindrance to the relative

movement of the metal ions to penetrate the large carboxylate groups in order to cross them may cause some shifts to take place very slowly [19] . Hence , the relaxation time will delay to some extent as is experimentally observed . The results of $\Delta\tau$ are summarized in Table III.3 . 2 .

Hence , the increase of the droplet density with time $d\rho/dt$ may be taken as a measure of the gel - growth . Thus ,

$$\frac{\rho_1 - \rho_2}{\Delta\tau} = k\,c \qquad (9)$$

where ρ_1 denotes the density of the electrolyte , ρ_2 the density of the sol , k is the rate constant of gel –growth and c is the proportional constant . Consequently , Eq . (9) may be simplified to yield ,

$$\frac{d\rho_1}{\Delta\tau} = kc \qquad (10)$$

The change of density of the metal electrolyte solutions (ρ_1) was used in Eq . (10) owing to the difficulty to measure the change in the droplet density as the gel growth proceeded .

Plots of ρ_1 against $\Delta\tau$ for different concentrations of metal ion electrolytes , gave good straight lines as shown in Figures III.3. (1 ~ 4). This linearity may indicate the validity of Eq . (10) for evaluating the rate constant of gel growth from the slopes of such lines ($d\rho_1/dt$) . Therefore , the values of ($\rho_1 - \rho_2$) $/\Delta\tau$ are considered as a measure of the exchange rate constant (k) ,i.e. the rate constant of

gel growth.[20] These values were calculated by the least –squares method and are summarized in Table III . 3 .3.

The rate of formation of the primary gel membrane was found to affect the relaxation time to a great extent . It has been found that the rates of formation of the primary membrane and the gel growth are high in metal ion electrolyte solutions of lower concentrations rather than in higher ones due to the high mobility of the metal ions in the former case . On the contrary , these rates are high in higher concentrations of sol rather than in that of lower concentrations owing to the presence of many exchange sites within the alginate macromolecular chains in the former sols in comparison with that of later ones . Hence , the relaxation time , $\Delta\tau$ decreases with increasing the concentration of the sol ; whereas it increases with increasing the metal ion concentration . In addition , the values of $\Delta\tau$ were found to decrease with increasing the temperature , which can be explained by the acceleration of the mobilities of the exchanged counter ions at higher temperatures .

The kinetic parameters for gel – growth were calculated from the dependence of the rate constant of gel growth (k) on temperature using both Arrhenius and Eyring equations , respectively [15, 16] . Plots of - ln k versus 1/T of Arrhenius equation were linear from whose slopes , the activation energies were obtained as shown in Figure III.3 . 5 . Again , plots of $-\ln \frac{h}{k_B T} k$ against 1/T of Eyring equation , gave good straight lines from whose slopes and intercepts , the enthalpies and entropies of activations were obtained as shown in Figure III.3. 6 . The kinetic parameters were calculated by using the method of least –squares and are summarized in Table III.3 . 4 .

The magnitude of the activation energy , $E_a^{\neq}$, observed in Table III.3 . 4 may reflect some information of the stability of these ionotropic gel complexes . The activation energies obtained indicated that the stability of these gels are increased in the order Sn $\simeq$ Pb < Cd < Hg alginates . This order was found to be in good consistent with that obtained from the thermal analysis of these complexes. [21] Moreover , the high negative values of entropy of activations observed are not surprising . This may be explained by the necessity of the small metal ions to penetrate the spaces of the interchange linkage of alginate macromolecule in order to crosslink the large carboxylate groups forming gel complexes, in an egg – box like structure.

Furthermore , in spite of the variety of nature of metal ion used , the free energies of activation seem to be not altered . This may indicate the similarity in the sol – gel transformation mechanisms for these gelation processes . Again. Plotting of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ values of the isokinetic relationship ($\Delta H^{\neq} = \alpha + \beta \, \Delta S^{\neq}$) [22, 23] was fairly linear with α =117 KJ mol^{-1} and β = 388 K as shown in Figure III.3 . 7 . The slight deviation observed for Sn – alginate may due to the small tendency of tin (II) to hydrolyze in aqueous solutions. [24] However , the β value obtained is significant and reflects the reactivity of these metal ions for gelation .

The experimental observations showed that each metal alginate gel complex has a characterized $\Delta\tau$ value depending on the density of metal ion electrolyte and temperature as shown in Table III.3 . 2 . As the exchange process between the metal and sodium counter ions proceeded , a simultaneous growth of the primary membrane is took place .

After the relaxation time interval has elapsed , the metal alginate droplet starts to sink into the electrolyte solution with an appreciable velocity (V) , depending on the mass , density , radius and size of the droplet as well as the density , pH and viscosity of the metal ion electrolyte .

Let us assume that there are three forces acting on the spherically shape alginate sol droplet . The first one being the weight of the droplet

$$F_1 = \frac{4}{3} \pi r^3 \rho_2 g \downarrow \qquad (11)$$

where r is the radius of the droplet which depends on the radius of the metal ion (r), and g is the gravitational force . The second force is the Archimedean force (F_2) , thus ,

$$F_2 = \frac{4}{3} \pi r^3 \rho_1 g \uparrow \qquad (12)$$

The third one is the dragging force (F_3) which depends on the viscosity of the medium (η) , radius and density of the droplet and increases with increasing the velocity of the falling droplet

$$F_3 = B m V \uparrow \qquad (13)$$

where m is the mass of the droplet and B is the proportional constant and equals

$$B = \frac{6\pi r \eta}{m} = \frac{9 \eta}{2 \pi \rho_2 r^2} \qquad (14)$$

The velocity of the falling droplet , V , is obtained from the slopes (V = dY / dt)of the corresponding experimentally determined Y-t curves . The experimental results are summarized in Table III.3 . 5 .

As the sol droplet gets in contact with the metal ion electrolyte , it floats just below the surface of the solution due to the smaller value of droplet density compared to that of electrolyte solution . At the beginning , the droplet velocity is equal to zero and , hence , the dragging force (F_3) can be omitted , i . e . ,

$$\frac{4}{3} \pi r^3 \rho_2 g < \frac{4}{3} \pi r^3 \rho_1 g \qquad (15)$$

As a result of exchange between Na^+ counter ions of the alginate sol and the metal ions , the density of the droplet will exceed that of the surrounding metal ion electrolyte (> $\Delta\tau$) and , hence , it starts to sink into the electrolyte solution with an appreciable velocity . The behaviour of sinking is controlled by the conditions

$$\frac{4}{3} \pi r^3 \rho_2 g > (\frac{4}{3} \pi r^3 \rho_1 g + 6\pi \eta r V) \qquad (16)$$

Equation (16) can be reformulated into the form

$$V < [(2 g r^2 (\rho_2 - \rho_1) / 9 \eta] \qquad (17)$$

Equation (17) requires that the velocity of the droplet (V) should be less than the factor $2 g r^2 (\rho_2 - \rho_1) / 9 \eta$, as is experimentally observed (Table III.3 . 5 .) .

It is well known that during sol – gel transformation, a considerable dehydration of the sol droplet takes place , leading to the formation of capillaries (see chapter II pages 55 and the references there in) . The dehydration process will affect the mass , size and radius of the droplet .

As shown in Table III.3. 6 , the density of the droplet and the density of the electrolyte are not the only determining factors of the relaxation time . Therefore , a mathematical treatment may be suggested to account the influence of diffusion controls on the relaxation time and velocity of acceleration . The equation of motion obeys the form

$$F = F_1 - F_2 - F_3 = F(m, V) = m \frac{dv}{dt} + V \frac{dm}{dt} \qquad (18)$$

Equation (18) leads to the following relationship

$$m \frac{dv}{dt} + (V - U) \frac{dm}{dt} = B - A m V \qquad (19)$$

where U is the velocity of the lost mass just after leaving the droplet the electrolyte surface and B is constant and can be defined by

$$B = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) g \qquad (20)$$

Assuming that the lost mass becomes immediately at rest after leaving the droplet (U =0) , hence Eq . (20) reduces to

$$\frac{dv}{dt} = B - \left(A + \frac{dm/dt}{m} \right) V \qquad (21)$$

The analysis of Eq . (21) can be completely understand if we consider the following assumptions

Case I :

Assuming that both the mass and density of the droplet are constants during the gelation process . Hence , Eq . (21) leads to

$$\frac{dv}{dt} = B - A V \qquad (22)$$

where

$$V = \frac{A}{B} \left(1 - e^{-Bt} \right)$$

Equation (22) requires the plots of dv / dt versus V to be linear with slopes (- A) and intercepts on dv / dt axis equals B which not agree with our experimental observations for dv /dt - V plots .

Case II :

If the mass of the droplet remains constant while its density is subjected to change as a result of the crosslinking of the interdiffused metal ions with the functional groups of the alginate macromolecules as well as the orientation of the solvent molecules and macromolecular chains toward these metal ions , plots of dv / dt versus V of Eq . (22) will give variables of A and B . This means that the term dv / dt is increased in magnitude than that expected in case I .

Case III :

If the density of the droplet remains constant , while its mass is subjected to change as a result of the outward reflux of water resulting from the dehydration process (shrinkage) , the value of A increases while that of B decreases . This fact may explained by the decrease occurred in dv / dt with the simultaneous increase in the term $\frac{dm / dt}{m}$ which has a negative sign .

As mentioned before , the velocity of acceleration can be determined from Y – t plots (V = dY / dt) . Then , the term dv / dt can be evaluated using the well – known graphical differentiation methods. [25 , 26] The result are summarized in Table III.3 . 7 . The plots of dv / dt against V are shown in Figures III.3. (8 and 9). This behaviour reveals that the changes in mass , density and radius of the droplet during the sol – gel transformation are rhythmic in nature , i . e behaves a pulsed manner .

The first part on $\frac{dv}{dt}$ -V plots represent the increase in velocity of acceleration of the falling droplet due to the diminishing in (r) and

corresponding increase of (ρ_2) or vice versa without any considerable change in the droplet mass (m) (case II) . The part at which no change in the dv / dt term may be explained by the simultaneous contraction of the radius and decrease in mass of the droplet in accordance to Stock's law .

Again , the sudden decrease in the velocity of acceleration of the droplet may be interpreted by the decrease in the droplet mass with the constancy of radius or density due to the dehydration process or shrinkage . (Case III) . The final increase in the velocity may be attributed to the gravitational acceleration .

Table III.3 . 1 : The distance covered by sinking the metal alginate gel droplets as a function of time .
$[M^{2+}] = 1.0$, $[Alg] = 0.1$ M (2 %) at 35 °C

Metal ion / Y , cm	Δτ , s			
	Cd^{2+}	Sn^{2+}	Hg^{2+}	Pb^{2+}
0	914	1185	1800	893
1	14	–	–	5
2	17	23	34	9
3	21	31	41	13
4	24	38	47	16
5	26	42	52	18
6	28	46	55	20
7	30	50	58	22
8	33	53	62	24
9	36	56	65	26
10	40	58	67	27
11	43	60	69	28
12	46	61	72	29
13	48	62	74	30
14	49	63	75	31

Experimental error ± 2 %

Table III.3 . 2 : Relaxation time as a function of the density of metal electrolyte solutions and temperatures .
[Alg] = 0.1 (2 %) , $[M^{2+}]$ = 1.0 M

Molarity M	Density g / cm^3	Δτ , S			
		25° C	35 ° C	45 ° C	55 ° C
Cd– alginate					
1.0	1.22	1165	914 (1645) *	720	547
0.5	1.10	587	466	371	285
0.25	1.05	307	244	196	152
0.125	1.02	162	131	107	84
Sn – alginate					
1.0	1.11	1401	1185 (2192)	975	739
0.5	1.06	722	602	497	379
0.25	1.03	374	312	259	198
0.125	1.02	197	164	137	106
Hg– alginate					
1.0	1.27	2303	1800 (3366)	1350	960
0.5	1.14	1177	905	682	490
0.25	1.07	602	471	357	259
0.125	1.04	345	253	193	142
Pb- alginate					
1.0	1.28	1085	893 (1661)	700	522
0.5	1.14	571	457	363	273
0.25	1.07	301	241	193	147
0.125	1.04	161	129	105	81

The values between brackets are obtained for 0.05M alginate (1 % w / v) .

TableIII.3.3: The rate of gel–growth for metal – alginate gel droplets (k).

$[M^{2+}] = 1.0$, $[Alg] = 0.1$ M (2 %)

Metal complex	10^4 d ρ_1 / Δ t s^{-1}			
	Temp , ° C			
	25	35	45	55
Cd - alginate	2.10	2.62	3.36	4.44
Sn – alginate	0.76	0.97	1.19	1.57
Hg – alginate	1.23	1.54	2.06	2.91
Pb – alginate	2.59	3.17	4.07	5.30

(r ± 0 .99)

Table III.3 . 4 : Kinetic parameters of gel growth for metal alginate gel droplets .

Parameter / Metal Complex	$Ea^{\neq}$ kJ / mole	$\Delta H^{\neq}$ kJ/ mole	$\Delta S^{\neq}$ J /mole K	$\Delta G^{\neq}_{298}$ kJ/mole
Cd – alginate	20.22	17.64	-256.29	94.01
Sn – alginate	19.15	16.95	-267.09	96.54
Hg – alginate	23.28	20.68	-250.68	95.38
Pb – alginate	19.42	16.84	-257.05	93.45

Experimental error ± 3 % for ($\Delta S^{\neq}$) .

Experimental error ± 1 % for ($\Delta H^{\neq}$) .

Table III.3. 5 : The values of V and $2 g r^2 (\rho_2 - \rho_1) / 9 \eta$ of metal alginate gel droplets .

$[M^{2+}] = 1.0$, $[Alg^-] = 0.1$ M (2 %) at 35 °C

Metal ions	Cd^{2+}	Sn^{2+}	Hg^{2+}	Pb^{2+}
V , $cm\ s^{-1}$	0.40	0.35	0.29	0.45
$2 g r^2 (\rho_2 - \rho_1) / 9 \eta$, $cm\ s^{-1}$	0.55	0.62	0.65	0.74

Table III.3 . 6 : Mass , density and radius of droplets as functions of $\Delta\tau$ and V for metal alginate gel droplets .
[Alg^-] = 0.1 (2 %) , [M^{2+}] = 1.0 M at 35 °C .

Metal ion	$\Delta\tau$/ s	m g	ρ_2 g / cm^3	r cm	V cm s^{-1}
Cd^{2+}	914	0.022	1.33	0.16	0.40
Sn^{2+}	1185	0.037	1.22	0.19	0.35
Hg^{2+}	1800	0.03	1.38	0.17	0.29
Pb^{2+}	893	0.020	1.39	0.15	0.45

Table III.3 . 7 : The values of V and dV / dt for metal alginate ge droplets .

[Alg] = 0.1 (2 %) , [M^{2+}] = 1.0 M at 35 °C .

Sn^{2+}		Cd^{2+}		Hg^{2+}		Pb^{2+}	
10 V cm s^{-1}	10^3 dV /dt	10 V cm s^{-1}	10^3 dV /dt	10 V cm s^{-1}	10^3 dV /dt	10 V cm s^{-1}	10^3 dV /dt
0.87	1.24	0.71	15.40	0.85	2.20	2.0	5.50
0.97	1.17	1.18	6.32	0.96	4.30	2.22	2.25
1.05	3.50	1.43	7.93	1.09	3.90	2.31	6.33
1.19	2.75	1.67	12.80	1.21	2.0	2.50	14.00
1.30	2.50	1.92	10.85	1.29	3.15	2.78	11.00
1.40	3.67	2.14	9.50	1.38	5.63	3.0	9.00
1.51	3.33	2.33	3.00	1.49	5.20	3.18	7.67
1.61	5.50	2.42	2.67	1.59	2.56	3.33	6.50
1.72	5.50	2.50	1.94	1.66	4.80	3.46	24.00
1.83	5.50	2.56	1.62	1.76	10.70	3.70	23.00
1.97	13.70	2.60	5.42	1.97	10.37	3.93	20.10
2.10	12.70	2.80	16.59	2.07	10.40	4.14	19.30

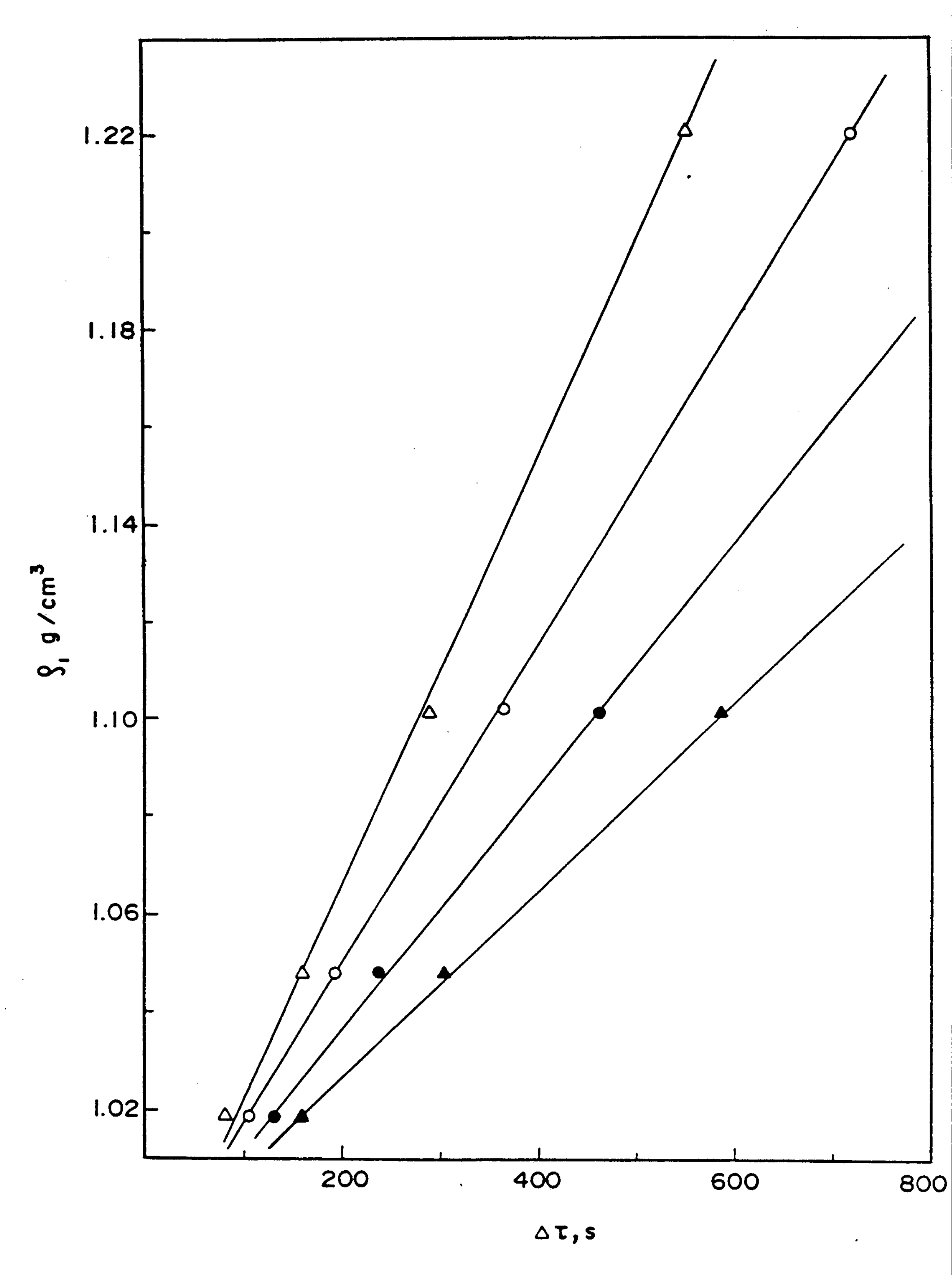


Figure.III.3.1: Plots of ρ_1 as a function of $\Delta\tau$ for [Cd^{2+}] - metal alginate gel droplet.

[Alg] = 2 %, [Cd^{2+}] = 1.0 M

[▲] : 25, [●]:35, [○] :45, [Δ] : 55 °C.

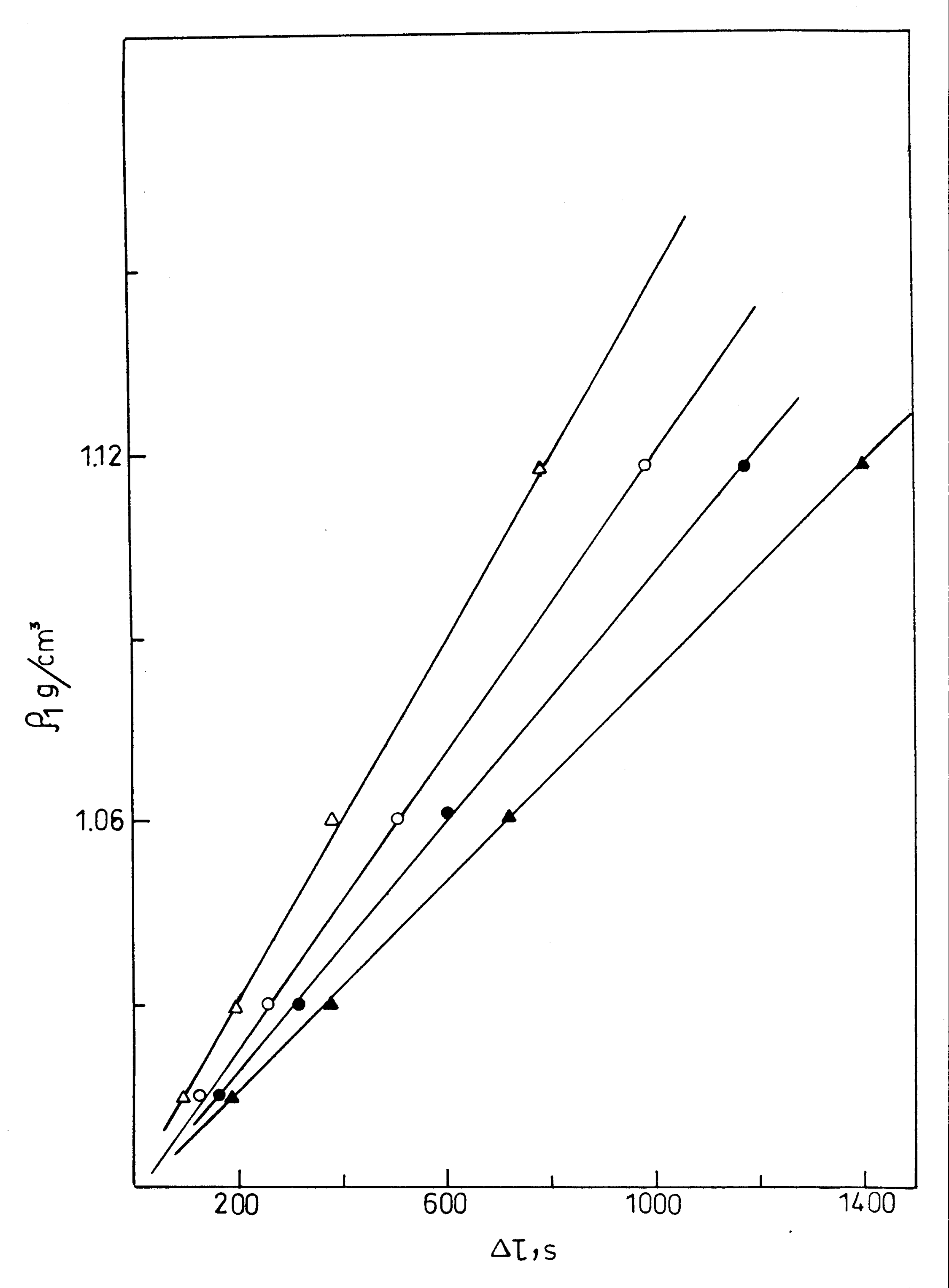


Figure. III.3.2: Plots of ρ_1 as a function of $\Delta\tau$ for[Sn^{2+}] - metal alginate gel droplet.

[Alg] = 2 %, [Sn^{2+}] = 1.0 M

[▲]: 25, [●]: 35, [○]: 45, [Δ]: 55 °C.

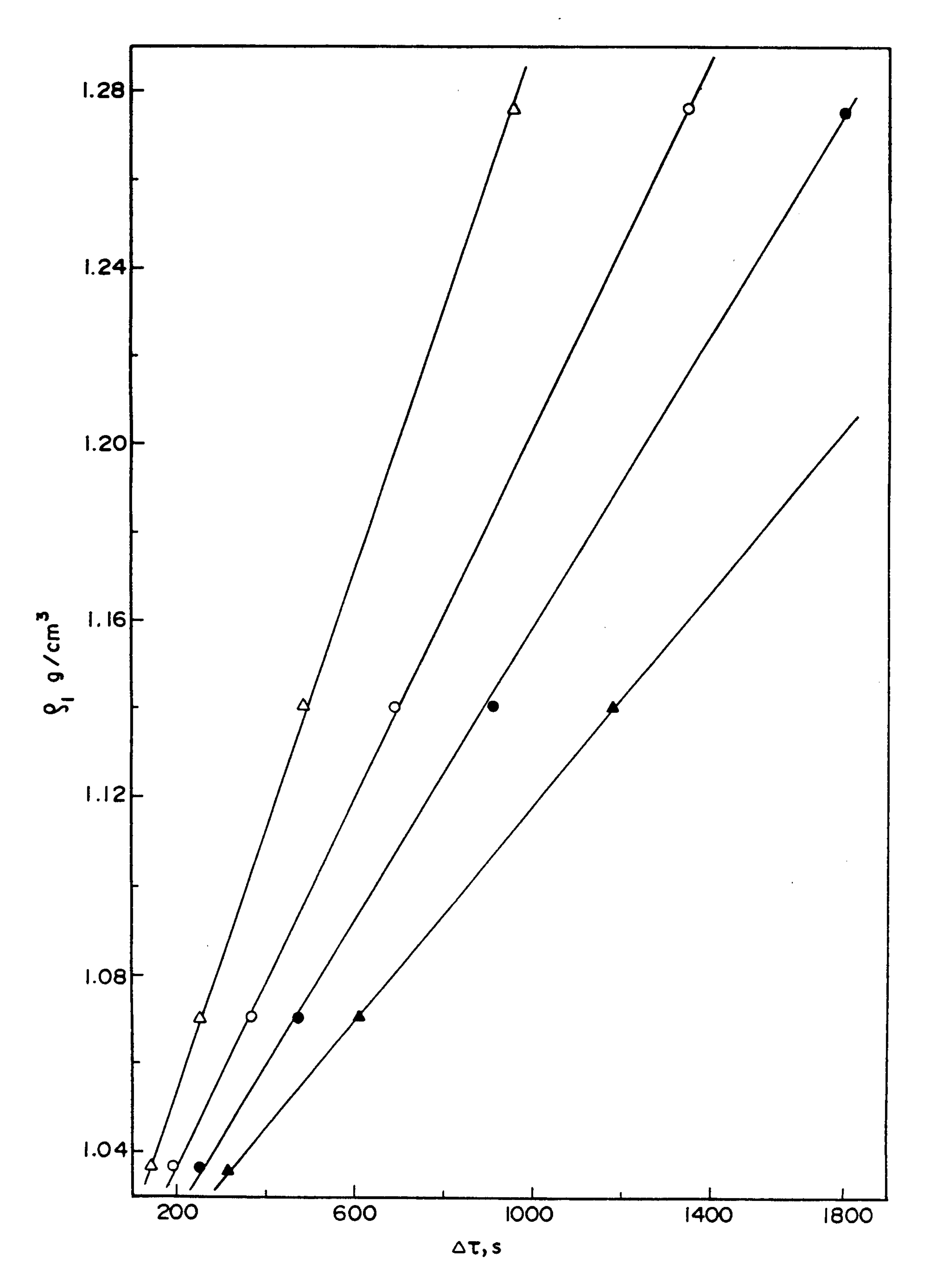


Figure. III.3.3 : Plots of ρ_1 as a function of $\Delta\tau$ for [Hg^{2+}]- metal alginate gel droplet .

[Alg] = 2 % , [Hg^{2+}] = 1.0 M

[▲]: 25, [●] :35, [○] :45 , [Δ] : 55 °C.

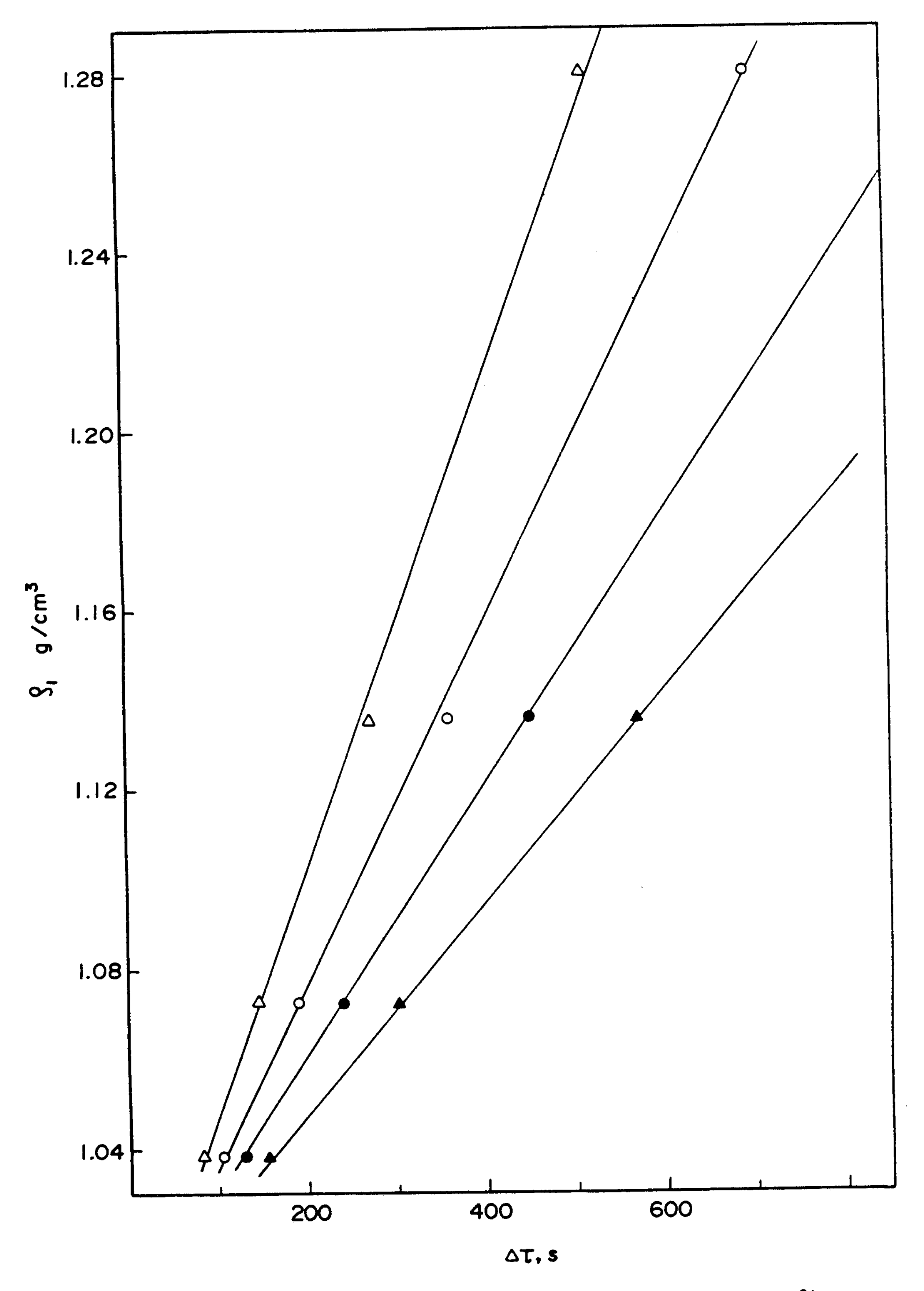


Figure. III.3.4: Plots of ρ_1 as a function of $\Delta\tau$ for [Pb^{2+}]- metal alginate gel droplet .

[Alg] = 2 % , [Pb^{2+}] = 1.0 M

[▲]: 25, [●] :35, [○] : 45 ,[Δ] : 55 °C.

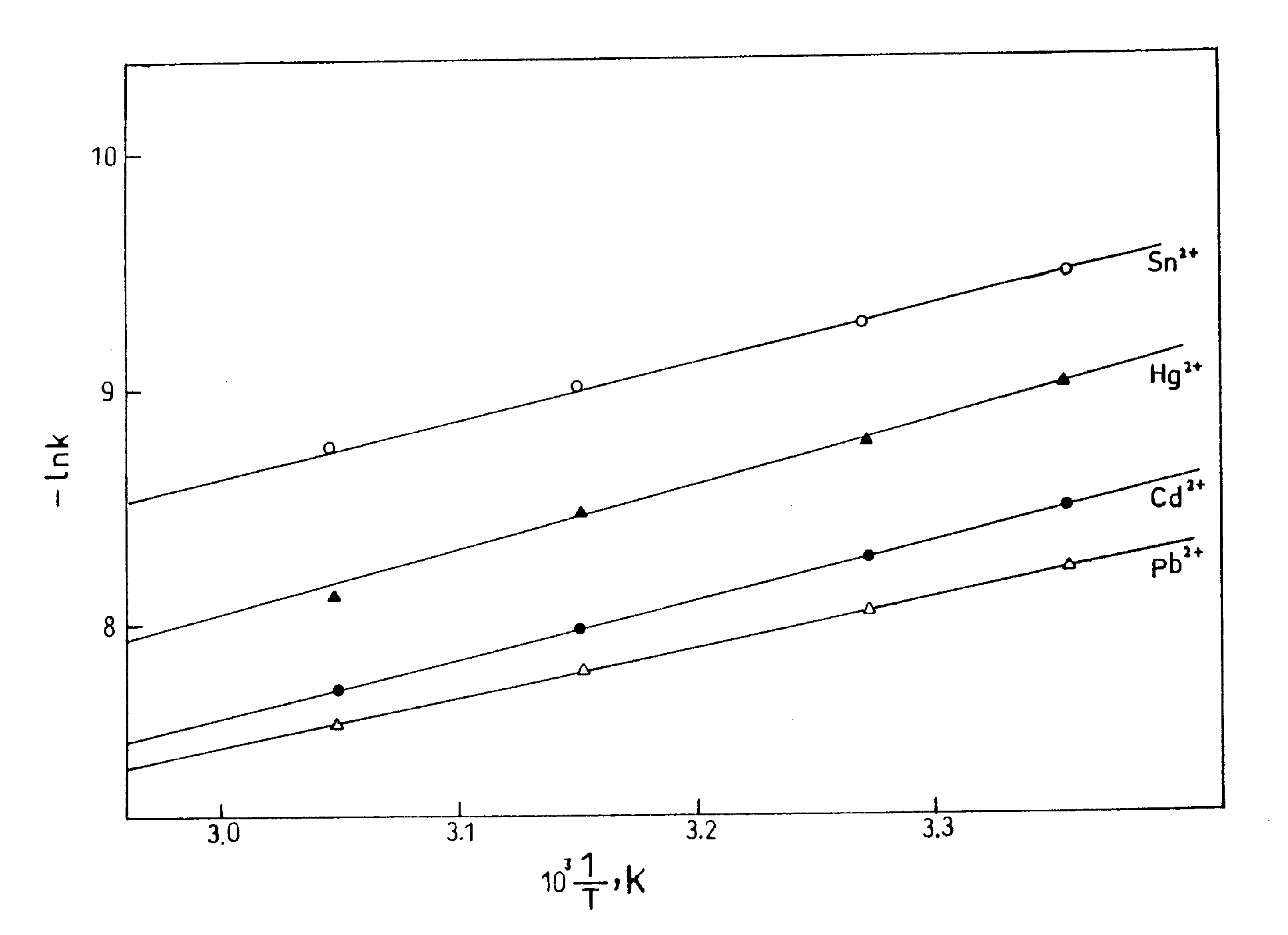


Figure. III.3.5: Arrhenius plots for metal alginate gels.

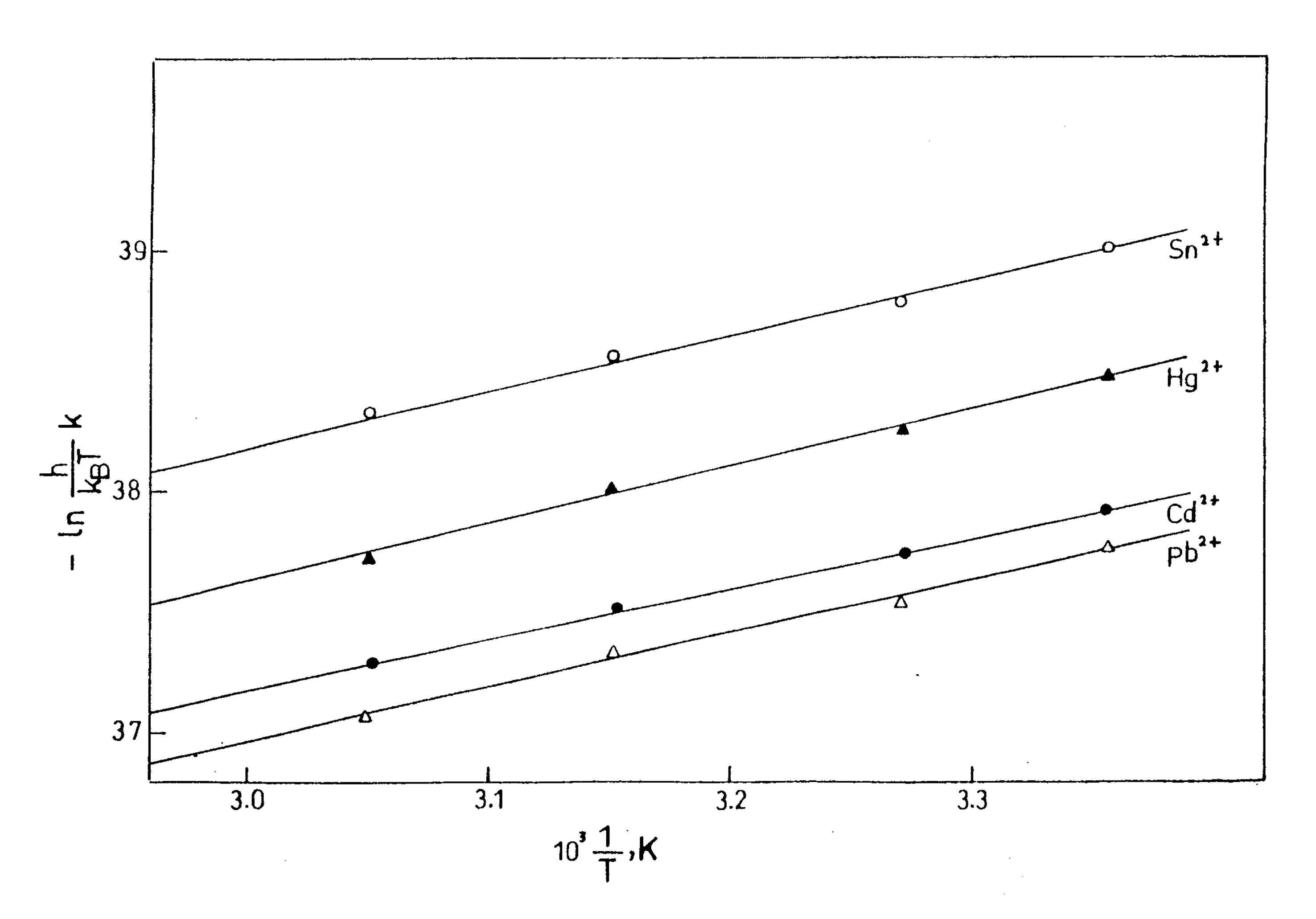


Figure. III.3.6: Eyring plots for metal alginate gels .

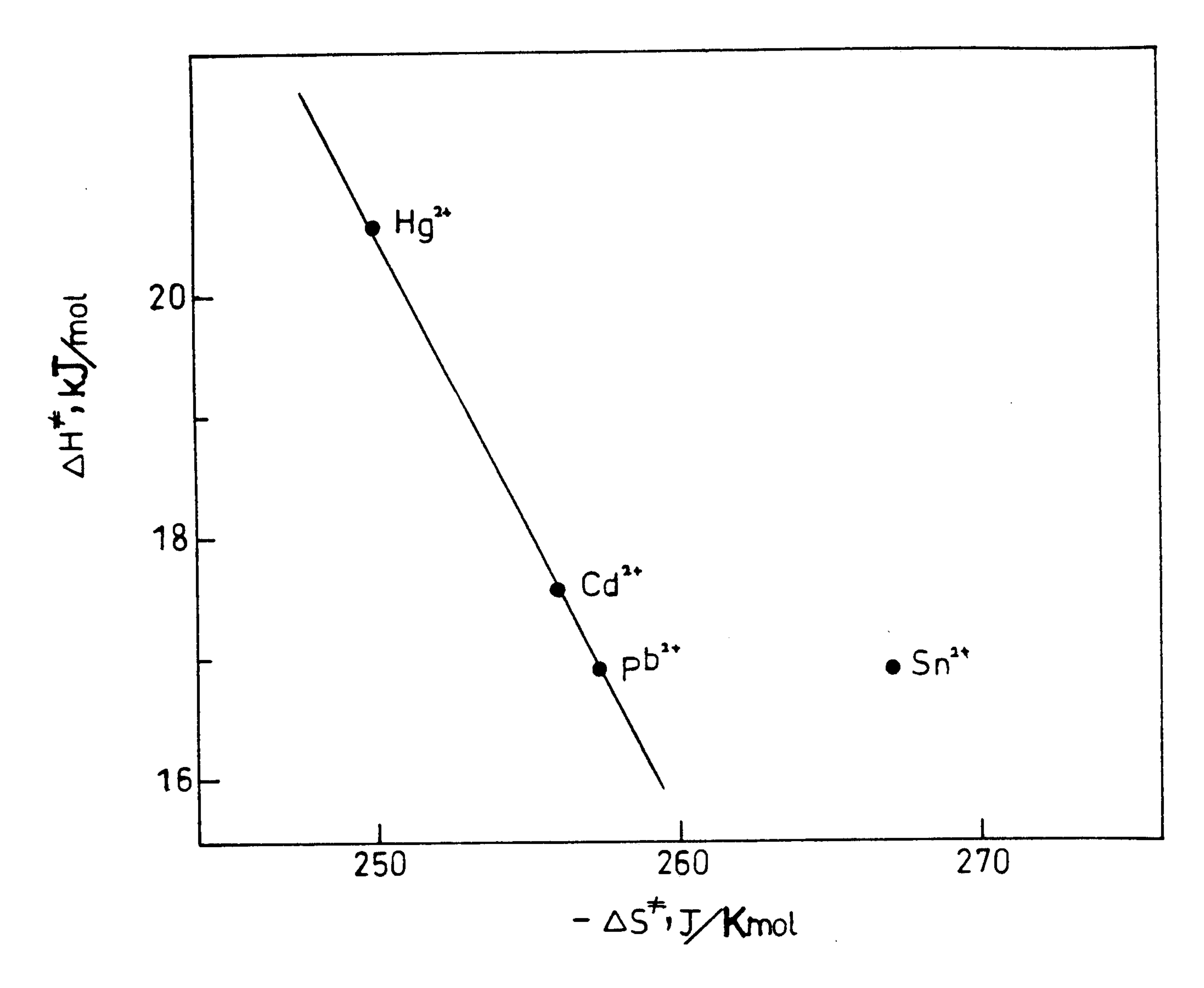


Figure. III.3.7:Isokinetic relationship plot for metal alginate gels.

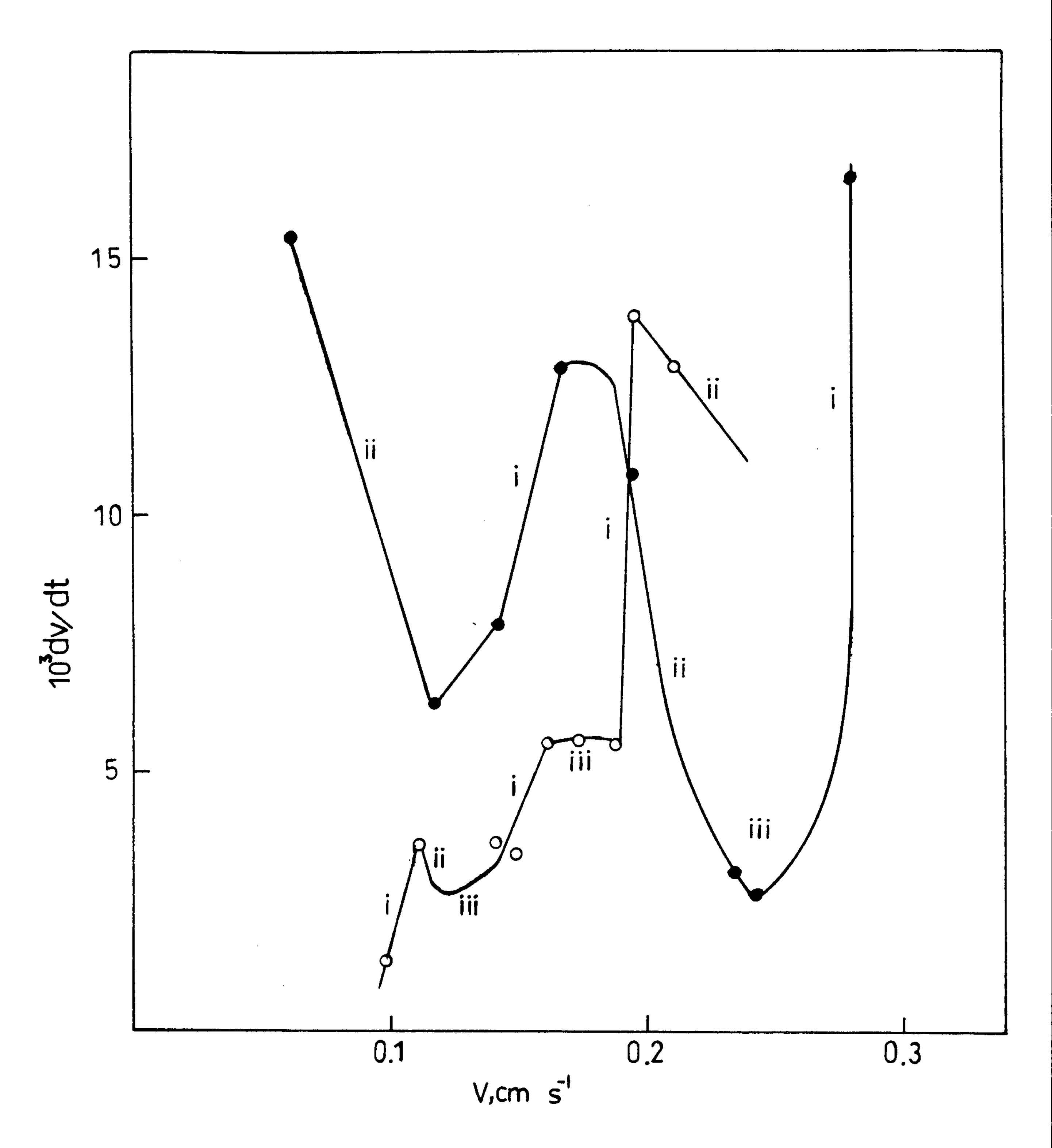


Figure.III.3.8:Plots of $\frac{dV}{dt}$ versus V for metal alginate gels .
[•]: Cd^{2+} ;[○] : Sn^{2+} at 35°C.

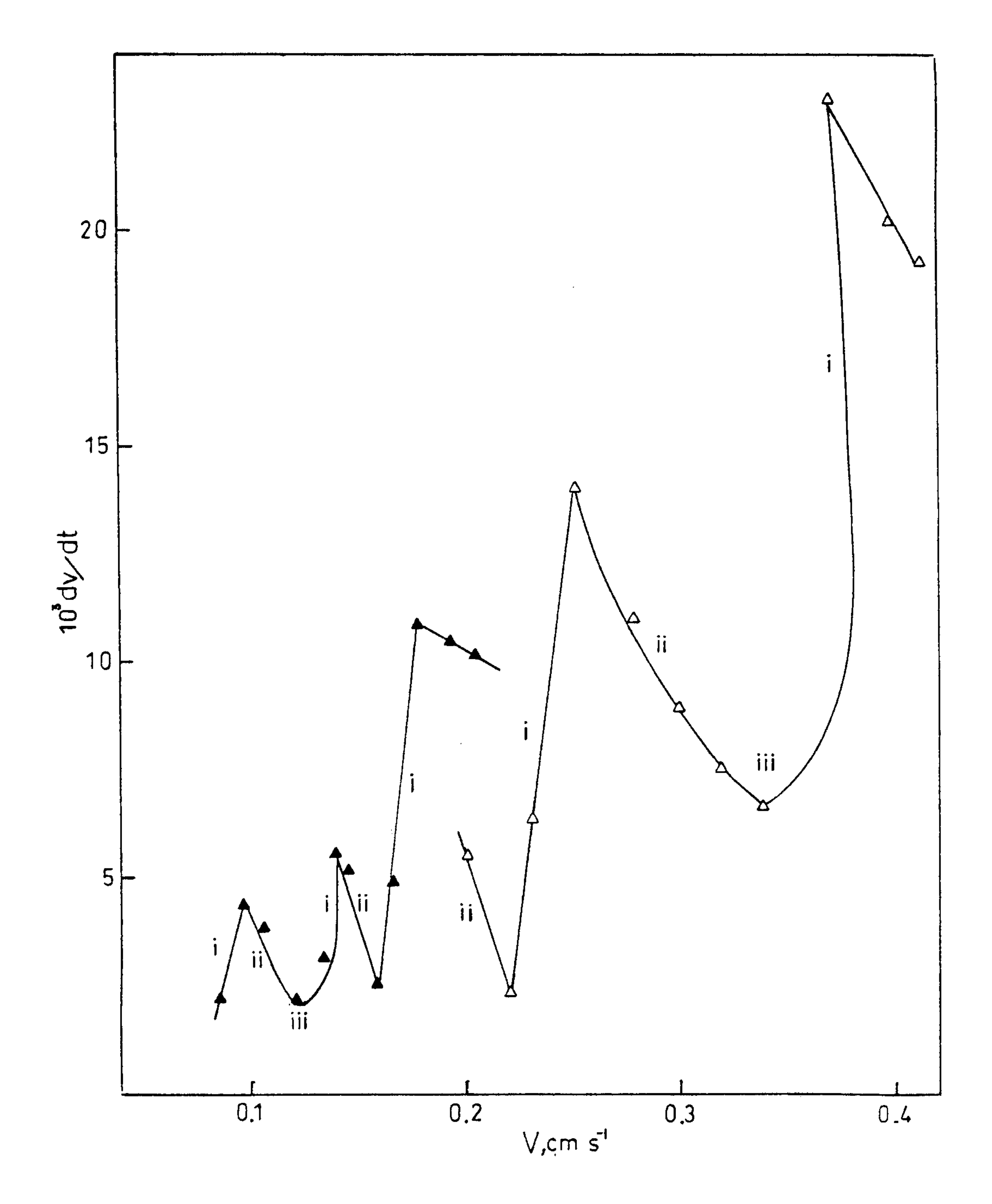


Figure.III.3.9: Plots of $\frac{dV}{dt}$ versus V for metal alginate alginate gels . [▲]:Hg^{2+} ; [Δ] : Pb^{2+} at 35 °C.

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CHAPTER IV

Kinetics and Mechanism of Sol –Gel Transformation between Sodium Alginate and Some Divalent Metal Ions With Formation of Capillary Ionotropic Polymembranes

IV . 1 . Introduction

IV. 1. Introduction :

Although , the literature reveals that considerable work has been done on ion exchange[1~5] , mechanical properties[6,7] , selectivity coefficients [8-11] , electrical properties [12~16] and the chromatographic separation [17~19] of metal alginate gel complexes , the kinetic studies on sol – gel transformation are still scarce .

In the preceeding chapter (III) , the drop density method has been applied to measure the rate of gel – growth for Sn (II)- ,Cd (II) - , Hg (II) –and Pb (II) – alginate gel complexes in the form of spherical pellets .

Awad et al . , investigated the rate of gel – growth for Cu(II)- [20] and Co(II)-[21] alginate gel droplets using both the droplet density and analytical methods .

Hassan and Coworkers studied the kinetics of sol – gel transformations for Ni(II)[22] ,Cu(II)[23] and Co(II) [24] metal ions with alginate sol using the analytical technique . When the metal ion concentration was present in a large excess over that of alginate sol, pseudo first order plots were sigmoidal in nature with two distinct stages . The initial part was fast and curved significantly at early times , followed by a decrease in the rate of gelation at longer times .

In view of the previous aspects , the present work has been undertaken using excess alginate sol concentration in order to obtain more information on sol – gel transformation mechanistics . The results which obtained may focus more light about the stability of the gel complexes in terms of the metal ion reactivity and the complex geometrical structure .

IV . 2.Experimental

IV .2.Experimental :

IV.2 – 1 . Materials :

All materials used were of analytical grade .Doubly distilled conductivity water was used in all preparations . The temperature was controlled within ±0.1°C

IV.2 – 2 .Preparations .

a – Preparation of Alginate Sol :-

Sodium alginate powder Cica Reagent (Canto Chem . Co .) was used in the preparation of alginate sols of different concentrations as described previously (chapter II P . 43)

b – Preparation of Metal Ion Electrolyte Solutions : -

Water – soluble salts of Cd (II) , Sn (II) ,Hg (II) and Pb (II) metal ions were used. Metal ion electrolyte solutions with various concentrations were prepared by dissolving the requisite amount of the reagent in bidistilled deionized water . The concentration of metal ions were carried out complexometrically against standard solutions of EDTA using the suitable indicator .

c - Preparation of EDTA Solutions :-

Ethylene diamine tetra acetic acid (disodium salt) was used in the preparations . The preparation and standardization of EDTA solutions were as described elsewhere. [25,26]

IV.2 –3 –Analyses of Electrolyte Solutions :-

a - Determination of Zn^{2+} cation concentrations :-

The zinc (II) concentration was determined by titration of zinc(II) using dimethylnaphthidine as follows :-

Reagents :- Standard solution of 0.1M EDTA ;1% $K_4Fe(CN)_6$;1%3,3- dimethylnaphthidine in acetic acid ; approx. 1M Na – acetal approx . 1M HCl.

Procedure :- To every 100 ml Zn (II) solution, a drop of ferrocyanide and 2-3 drops of naphthidine are added , followed by 3 ml of sodium acetate and about 0.5 ml HCl .The pH of the mixture should be between 5 and 6 and the colour should be a violet red . Titration with EDTA is now carried on until the colour begins to become decidedly weaker .

b- Determination of Cd^{2+} cation concentrations :-

The cadmium (II) concentration was determained by a direct titration of cadmium with xylenol orange as indicator as follows :-

Reagents :- Standard 0.005 M – EDTA ; hexamine , xylenol orange.

Procedur:- The sample solution is adjusted to pH 5 by adding a few amount from hexa - mine . Xylenol orange is added where a red colour should appear .Titration with EDTA is carried out until the colour begins to become yellow .

c - Determination of Pb^{2+} cation concentrations :-

The lead (II) concentration was determined by a direct titration of lead using Erichrom black T (Erio T) as follows :-

Reagents : - Standard 0.01 M EDTA ; Erio T ; pH 10 buffer ;1M Na – K tartrate ; if necessary KCN as a masking agent .

Procedure :- The sample solution is treated with 5 ml of tartrate or 1 : 4 triethanolamine and made approximately neutral with NaOH . If necessary a masking agent such as KCN is added at this stage . Then 2 ml of buffer and indicator are added and the titration carried out until the colour change from red to blue.

IV.2-4- Kinetic Measurements :-

Preliminary experiment indicated that the rate of sol – gel transformation is altered by changing the metal ion and alginate concentrations . From this point of view , the kinetics were performed under pseudo first – order conditions where $[Alg^-]_o >> [M^{2+}]_o$. The alginate sol and the metal ion electrolyte were equilibrated at the desired temperature in a thermostated water – bath . After the reactants had attained the temperature of the water – bath , fixed known volume of the alginate sol was poured inside the column , followed by a careful addition of the metal ion electrolyte using a syringe or pipette on the internal walls of the column to avoid the deterioration of alginate sol surface . The time of contact of the metal ion electrolyte with the sol surface was recorded . After known time intervals , known volumes of the metal ion electrolyte solution were pipetted out and the variation of its concentration as a function of time was followed complexometrically . Before each run a current of air is bubbled in the electrolyte solution to avoid the concentration gradient resulting from the exchange process of the counter ions across the membrane formed between the alginate sol and the electrolyte solution of the metal ion .

It noticed that the observed rate constants of gelation , k_{obs} , are not in agreement with the suggested rate law expression at the high concentrations of alginate sol ($[Alg^-]_o > 0.12M$) . This may be explained by the marked dependence of

alginate viscosity on the sol concentration . Thus in turn leads to retard the exchange process between the two exchanging counter ions . Again , in alginate sols of higher concentrations , there is a large number of exchangeable Na^+ counter ions which leading to longer times of exchange process . Therefore , all of the experimental runs in the present work were performed at $[Alg^-]_o < 0.12$ M .

Some kinetic measurements were performed conductimetrically to check the complexometric results . The values for the change in concentration obtained from the conductimetric runs were found to be in good agreement with that observed complexometrically within the experimental error (±3%) . This fact indicates that the results obtained are reliable . The results are summarized in Tables IV.3 (1~6) .

IV .3 . Results and Discussion

IV . 3 . Results and Discussion :-

IV.3.1. Stoichiometry :-

The stoichiometry of ion exchange requires that the fluxes of the two exchanging counter ions be equal in magnitude , eventhough the counter ion mobilities may be quite different . Therefore , any counter ions which leave the alginate macromolecule chains (Na^+) must be replaced by an equivalent amount of divalent metal ions. [27,28]

The stoichiometry of the overall gelation process was determined complexometrically in the presence of excess metal ion concentration over that of alginate sol . The unreacted metal ion concentration was estimated periodically till it had reached a constant value, .i.e, completion of reaction , at room temperature . Stoichiometric ratios 0.52 ± 0.03($[M^{2+}]_{consumed} / [Alg^-]_o$) were obtained at several initial concentrations of metal ions . Unfortunately , no method could be devised which was specific for alginate sol determination. The stoichiometry of such gelations processes can be expressed by the following exchange reaction .

$$2\,(\text{Na-Alg})_n + M^{2+} = (M-\text{Alg}_2)_n + 2\,Na^+ \quad (1)$$

sol electrolyte gel electrolyte

where Na–Alg denotes the sodium alginate , $M\text{–}Alg_2$ is the metal alginate gel complex and M is the metal ion .

IV.3-2. Dependence of Gelation Rate Constant on [Alg] and [M^{2+}] :

The order with respect to reactants was determined by working under pseudo – first order conditions with [Alg^-] in a large excess over that of the metal

ion electrolyte . The concentration of Alg^- sol was varied from 0.025 to 0.1 M , whereas [M^{2+}]suitable for the kinetic measurements was kept as (4~6) x 10^{-3} M . Plots of Ln ($c_t - c_\infty$) vs time were found to curve significantly at early times but became linear and relatively slow at longer times (where c_t =(a – x)) . Typical plots are shown in Figures IV.3.(1~6) . These curves indicate that the gelation reaction obeys the expression

$$-(C_\infty - C_t) = B_o e^{R_f t} + P_o e^{-R_s t} \qquad (2)$$

where R_f and R_s are the first – order rate constants of exchange for the fast and slow gelation steps , B_o and P_o represent the initial concentration of the sol in the two gelation processes and C_t and C_∞ are the concentrations of metal ion at time t and infinity , respectively . The rate constants of exchange were obtained by drawing a straight line through the fast linear portion (R_f) of the first order plot and extrapolating the line back to zero time (B_o) . The rate constant of exchange , R_s for the slower gelation reaction can be obtained from plots of the form ln [(C_∞ -C_t) -(C_∞ -C_t)] vs time . The quantity (C_∞-C_t) represent the experimental point and (C_∞-C_t) represents the extrapolated point at time t. [29,30] This behaviour is quite similar to that observed in the gelation reactions reported earlier. [22~24] Therefore , the present work is concerned with the relatively fast initial parts , since the second stage is too slow . The second – order rate constants of gelation were obtained by dividing the observed first – order rate constants by alginate concentration ($R_g = R_f$ (or R_s)/ $[Alg^-]_o$. The constancy obtained indicates that the rate of gelation is also first – order in alginate concentration . The rates of

gelation were calculated by the least – squares method and are summarized in Tables IV.3.(7 and 8) .

IV.3.3.Dependence of Gelation Rate Constant on Temperature :-

The kinetic parameters of the sol- gel transformations were investigated by studying the gelation processes at various temperatures ranging between 35 and 65 °C . The kinetic parameters were determined from the dependence of the rate constant of gelation on temperature using Arrhenius[31] and Eyring [32] equations and are summarized in Table IV.3.9. Plots of $-\ln R_G$ against 1 / T of Arrhenius equation gave good straight lines from whose slopes , the activation energies were obtained as shown in Figure IV.3.7. Again , plots of $-\ln \frac{h}{k_B T} R_G$ versus 1 / T of Eyring equation were fairly linear from whose slopes and intercepts the enthalpies and entropies of activation were determined , respectively as shown in Figure IV.3.8. These values were calculated by the least – squares method and are summarized in Table IV.3.10.

IV.3.4.Mechanism of Gelation :

As a divalent metal ion gets in contact with alginate sol , a primary membrane will be formed on the surface of the sol on immediate contact with the electrolyte . This membrane will separate the sol from the surrounding electrolyte , whereas the macromolecular chains of alginate polyelectrolyte start to distribute themselves statistically below the already formed primary membrane . As a steady- state condition is established , the Na^+ counter ions began to migrate from the alginate sol outward into the electrolyte solution through the primary membrane . Simultaneously , the metal ions must go inward and occupy the places left by Na^+ ions . The net process is a transfer of ions in both the sol

and the electrolyte .[22~24] When the metal ions are allowed to diffuse upward , non capillary gel membranes are formed . This method of gel preparation is known as the ascending technique .When the metal ions diffused in the downward direction , capillaries that are straight , parallel and nearly identical to each other in the direction of diffusion between the Na^+ and metal ions are formed . This method of gel preparation is termed the descending technique . Under microscopic investigation , these capillaries appear as fine pores of the same radius in a transverse section. [33,34] The diameter of these pores depends on several factors such as the ionic radii of the interdiffused metal ion , the pH of the electrolyte , the concentration of the alginate sol and the orientation of the coordinated water molecules toward the chains of the alginate macromolecule toward the chelated metal ion. [35] The width of these capillaries may play a role in the rate of exchange process . In either ascending or descending techniques , the diffusion process takes place stepwise and the continuity of such diffusion leads to the formation of multilayer ionotropic membranes . Hassan and coworkers succeeded to separate these polymembranes into monolayers. [35]

In these ionotropic polymembrane gels , the interdiffused metal ion chelate the functional groups of the alginate macromolecular chains . A sort of bridge between two carboxylate groups and one or two pairs of hydroxyl groups is formed depending on the coordination number of the metal ion .[36] Two geometrical structures were suggested. [37] The first corresponds to an interamolecular association in which the functional groups involved in chelation belong to the same chain . Hence , the plane involving the chelated metal ion is parallel with the plane of the alginate macromolecular chains . This configuration is called planar geometry . The second type of geometry represents to the intermolecular

association in which the plane containing the metal ion is perpendicular to the plane of alginate macromolecular chains . In the later case , the functional groups are related to different chains and the configuration is termed by non – planar geometry . The two geometrical structures are illustrated in Scheme (I) . The priority of the two geometrical structures depends on the geometrical stability of the metal gel complex obtained .

The relatively fast initial part is explained by the rate of primary gel membrane formation . The second slow part seems to be controlled by the compactness of the network of the already formed gel membrane which depends on the alginate sol concentration and temperature . In exchange reactions , two possible rate determining steps have been considered . There are the counter ion exchange across the interface between the alginate sol and the metal ion electrolyte [38] and the actual exchange reaction at the fixed ionic groups. [39~41] Rate control by ion exchange across the interface is unlikely. [42] It is worthwhile to consider the exchange of the interdiffused ions in either fast or slow gelation steps as the rate controlling . The magnitude of the activation energy values obtained (Table IV . 3 . 10) may support this suggestion .

It is noticed that the rate constants of gelation were in the order Pb > Cd > Zn – alginates as shown in Table IV.3.8. The magnitude of the rate constants depends on the ionic radii of the interdiffused metal ions as well as the density of their electrolytes . Lead (II) electrolyte is known to have the greatest density [43] and so the largest rate of gelation . A plot of -ln Rg against the density of electrolyte was linear as shown to Figure IV.3.9. Again , Zn (II) in is the smallest [43] and hence possesses the lowest rate of gelation . A plot of -ln Rg vs . the ionic radii was also linear as shown in Figure IV.3.10.

Furthermore , the large negative entropy of activation observed can be interpreted by the necessity for these small metal ions to penetrate the large carboxylate groups in order to bring them together and form the ionotropic gel polymembranes . It was found that the orientation of the macromolecular chains and solvent molecules toward the metal ions are strongly influenced the kinetic parameters of sol –gel transformations and tend to affect the entropy of activation . Since the entropy of activation increases with decreasing orientation factor , the magnitude of orientation should be in the order Cd < Pb < Zn – alginate .[44,45] This is consistent with the values of entropies of activation for these gel polymembranes . In spite of the variety of the metal ions used , it seems that the free energy of activation remained unaltered . This fact may suggest that the mechanisms of the sol – gel transformation of these metal – alginates are nearly similar .

The kinetic parameters for some gelation reactions which possess negative entropies of activation are also summarized in Table IV.3.11 . Lefler and Granwald [46] have pointed out that many reactions show isokinetic relationship given by $\Delta H^{\neq} = C + \beta \Delta S^{\neq}$. As show in Figure IV.3.11 . A plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for some gelation reactions is fairly linear , with $C = 94$ k J mol^{-1} and $\beta = 301$ K . This linearity indicates that these sol – gel transformations follow similar mechanisms . Also , the β value obtained is significant and may be considered as a deserved comment .

The rate constants of gel – growth obtained by the drop density method in chapter III were found to be in the same order of magnitude with that obtained , in the present study, kinetically . This may confirm the producibility of the results obtained .

Table IV.3.1: The change of concentration of $[Zn^{2+}]$ as a function of time at constant $[Alg]_o$ for the fast initial and slow final-stages of gelation.

$[Alg] = 5.05 \times 10^{-2}$, $[Zn^{2+}] = 6.2 \times 10^{-3}$ M.

-ln C_t				
Temp, °C / Time,min	35	45	55	65
Fast –stage				
5	–	–	–	–
10	–	–	5.140	5.147
20	5.115	5.115	5.148	5.160
40	5.123	5.125	5.162	5.178
60	5.130	5.135	5.176	5.195
100	5.143	5.153	5.203	5.230
150	5.161	5.178	5.240	5.278
200	5.178	5.203	5.273	5.315
Slow –stage				
300		5.213		
400		5.222		
500		5.231		
600		5.236		
700		5.245		
800		5.252		

Table IV.3.2:The change of concentration of $[Zn^{2+}]$ as a function of time at variable $[Alg]_o$ for the fast initial stage of gelation.

$[Zn^{2+}] = 6.2 \times 10^{-3}$ M at 45 °C.

-ln C_t			
$[Alg]_o$,M / Time.min	2.52×10^{-2}	7.58×10^{-2}	10.10×10^{-2}
Fast stage			
5	–	5.130	5.160
10	–	5.135	5.165
20	–	5.142	5.171
40	5.115	5.156	5.186
60	5.112	5.170	5.200
100	5.130	5.177	5.231
150	5.145	5.231	5.278
200	5.158	5.265	5.350

Table IV.3.3: The change of concentration of [Cd^{2+}] as a function of time at constant $[Alg]_o$ for the fast initial and slow final stages of gelation.

[Alg] = 5.05 x 10^{-2}, [Cd^{2+}] = 4.0 x 10^{-3} M.

	-ln C_t			
Temp.°C / Time.min	35	45	55	65
Fast-stage				
5	-	5.563	5.573	5.627
10	5.521	5.573	5.583	5.655
20	5.545	5.599	5.618	5.776
40	5.565	5.627	5.699	5.971
60	5.585	5.684	5.578	5.166
100	5.620	5.745	5.933	5.438
150	5.667	5.843	6.119	5.850
200	5.710	5.935	6.384	7.205
Slow-stage				
300		6.02		
400		6.06		
500		6.10		
600		6.14		
700		6.17		
800 .		6.20		

Table.IV.3.4: The change of concentration of $[Cd^{2+}]$ as a function of time at variable $[Alg]_o$ for the fast initial stage of gelation. $[Cd^{2+}] = 4 \times 10^{-3}$ M at 45 °C .

	- ln C_t		
$[Alg]_o$, M / Time , min	2.52×10^{-2}	7.58×10^{-2}	10.10×10^{-2}
Fast stage			
5	–	5.626	5.683
10	5.621	5.635	5.713
20	5.626	5.656	5.743
40	5.647	5.712	5.815
60	5.665	5.744	5.885
100	5.705	5.865	6.044
150	5.751	5.995	6.225
200	5.798	6.194	6.411

TableIV.3.5:The change of concentration of $[Pb^{2+}]$ as a function of time at constant $[Alg]_o$ for the fast initial and slow final -stages for gelation.

$[Alg] = 5.05 \times 10^{-2}$, $[Pb^{2+}] = 3.85 \times 10^{-3}$ M .

	-ln C_t			
Temp..°C / Time,min	35	45	55	65
Fast - stage				
5	5.62	5.64	5.74	5.77
10	5.63	5.66	5.76	5.80
20	5.64	5.68	5.78	5.83
40	5.66	5.72	5.85	5.89
60	5.69	5.76	5.91	5.95
100	5.75	5.84	6.03	6.13
150	5.82	5.94	6.16	6.28
200	5.88	6.03	6.31	6.40
Slow –stage				
300		6.10		
400		6.14		
500		6.18		
600		6.22		
700		6.26		
800		6.30		

Table IV.3.6: The change of concentration of $[Pb^{2+}]$ as a function of time at variable $[Alg]_o$ for the fast initial stage of gelation

$[Pb^{2+}] = 3.85x10^{-3}$ M at 45°C.

	-Ln C_t		
$[Alg]_o$,M / Time,min	$2.52 x10^{-2}$	$7.58 x10^{-2}$	$10 .10x10^{-2}$
Fast – stage			
5	5.54	5.72	5.78
10	5.55	5.74	5.80
20	5.56	5.76	5.80
40	5.58	5.82	5.93
60	5.60	5.87	6.01
100	5.64	6.01	6.16
150	5.69	6.16	6.36
200	5.74	6.30	6.56

Table IV.3.7: The observed pseudo first – order (R_f) and second order (R_g) rate constants for the fast initial stage of gelation .

[Alg⁻] = 5.05 x10^{-2} , [M^{2+}] =(4~6) X 10^{-2}M

Metal ion	Zn^{2+}		Cd^{2+}		Pb^{2+}	
Rates / Temp °C	$10^5 R_f$ s^{-1}	$10^4 R_G$ $m^{-1}s^{-1}$	$10^5 R_f$ s^{-1}	$10^4 R_G$ $m^{-1}s^{-1}$	$10^5 R_f$ s^{-1}	$10^4 R_G$ $m^{-1}s^{-1}$
35	0.58	1.15	1.59	3.15	2.25	4.46
45	0.79	1.57	3.18	6.30	3.30	6.53
	(0.14)[a]	(0.27)[a]	(0.60)[a]	(1.20)[a]	(0.68)[a]	(1.34)[a]
55	1.17	2.31	6.78	13.43	4.85	8.08
65	1.47	2.91	14.02	27.76	5.38	10.64

a .The values between brackets for the slow final stage of gelation .

Experimental errors (± 2 %)

TableIV.3.8: Dependence of rate constants of gelation on alginate concentration for the fast initial stage of gelation. $[M^{2+}] = (4\sim6) \times 10^{-2}$ M at 45 °C.

Metal Ion	Zn^{2+}		Cd^{2+}		Pb^{2+}	
Rate / [Alg], M	$10^5 R_f$ s^{-1}	$10^4 R_g$ $m^{-1} s^{-1}$	$10^5 R_f$ s^{-1}	$10^4 R_g$ $m^{-1} s^{-1}$	$10^5 R_f$ s^{-1}	$10^4 R_g$ $m^{-1} s^{-1}$
2.53	0.39	1.54	1.57	6.22	1.68	6.65
5.05	0.79(0.74)[a]	1.57	3.18(3.09)[a]	6.30	3.30(3.22)[a]	6.53
7.58	1.15	1.51	4.71	6.21	5.01	6.59
10.10	1.55	1.55	6.19	6.13	6.65	6.58

a .The values between brackets were obtained conductimetrically .

Experimental errors (± 2 %)

Table IV.3.9: The values of $-\ln Rg$ (a) and $-\ln \frac{h}{k_B T} Rg$ (b) of Arrhenius and Eyring equations as functions of the reciprocal temperature for the fast initial stage of gelation.

T ,K	308	318	328	338
10^3 1/T ,K^{-1}	3.25	3.15	3.05	2.96
Zn(II)-alginate	a)9.07	8.76	8.37	8.14
	b)38.56	38.28	37.93	37.73
Cd(II)-alginate	a)8.06	7.37	6.61	5.89
	b)37.55	36.89	36.17	35.47
Pb(II)- alginate	a)7.72	7.33	7.12	6.85
	b)37.21	36.86	36.67	36.43

Table IV.3.10: The kinetic parameters of gelation reactions for the fast initial stage.

Parameter / Metal Complex	$E_a^{\neq}$ $kJmol^{-1}$	$\Delta H^{\neq}$ $kJmol^{-1}$	$\Delta S^{\neq}$ $JK^{-1}\ mol^{-1}$	$\Delta G^{\neq}_{298}$ $kJmol^{-1}$
Zn(II)- alginate	27.50	24.79	-240.09	96.34
Cd(II)-alginate	62.99	60.34	-116.56	95.68
Pb(II)- alginate	24.46	21.80	-238.29	92.81

Experimental errors ± 3 % for ($\Delta S^{\neq}$).

Experimental errors ± 1% for ($\Delta H^{\neq}$).

TableIV.3.11:Kinetic parameters of some gelation reactions for the fast initial Stage .

Metal Alginate	$\Delta S^{\neq}$ $Jmol^{-1} K^{-1}$	$\Delta H^{\neq}$ $kJmol^{-1}$	$\Delta G^{\neq}$ $kJmol^{-1}$	Ref.
Co^{2+}	-260.89	14.77	92.50	18
Ni^{2+}	-224.49	25.29	92.19	19
Cu^{2+}	-176.64	37.80	90.44	20
Zn^{2+}	-240.09	24.79	96.34	This work
Cd^{2+}	-116.56	60.34	95.68	This work
Pb^{2+}	-238.29	21.80	92.81	This work

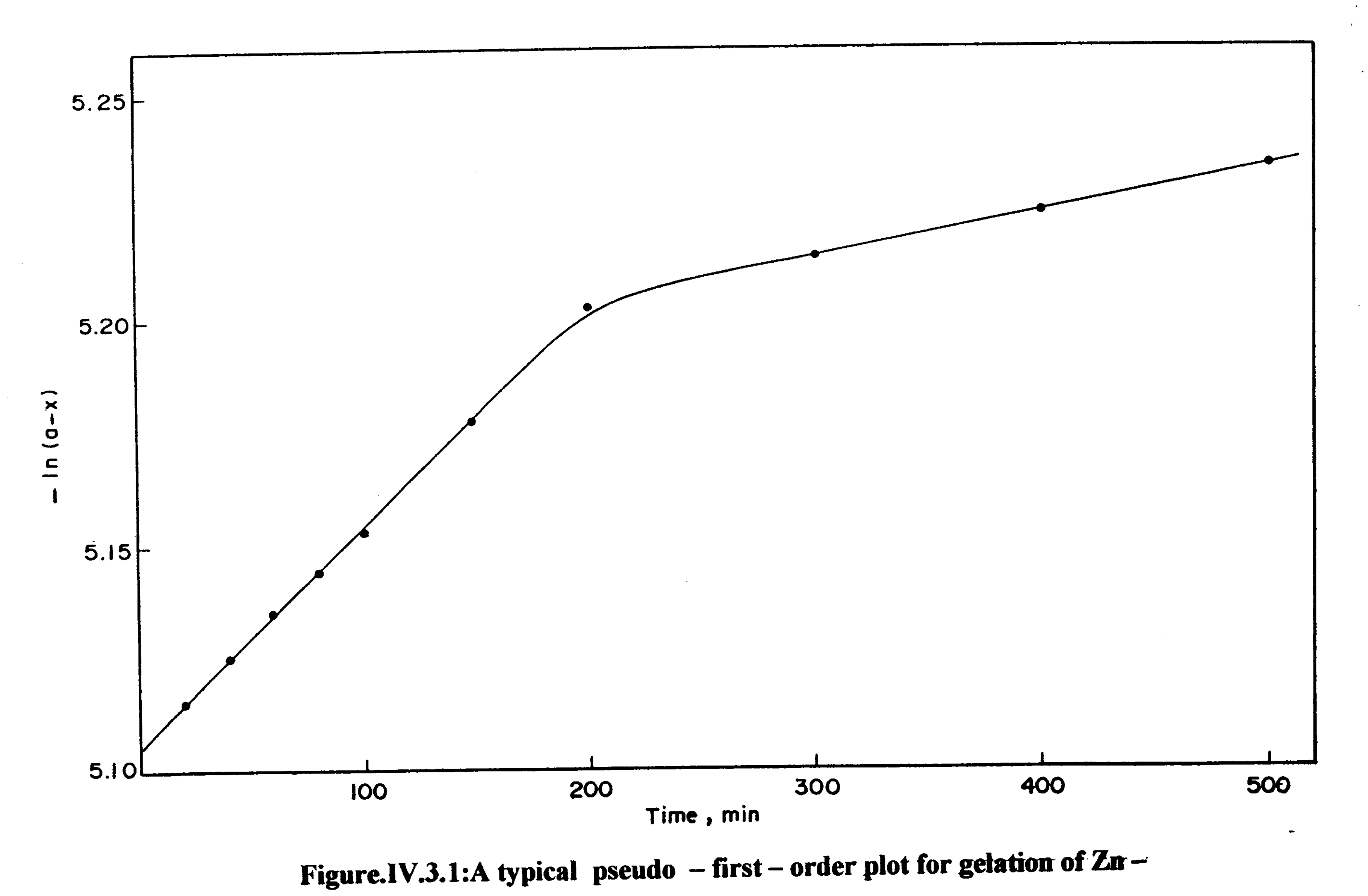


Figure.IV.3.1:A typical pseudo – first – order plot for gelation of Zn – alginate gel complex .
$[Alg] = 5 \times 10^{-2}$, $[Zn^{2+}] = 6.2 \times 10^{-3}$ M at 45 °C .

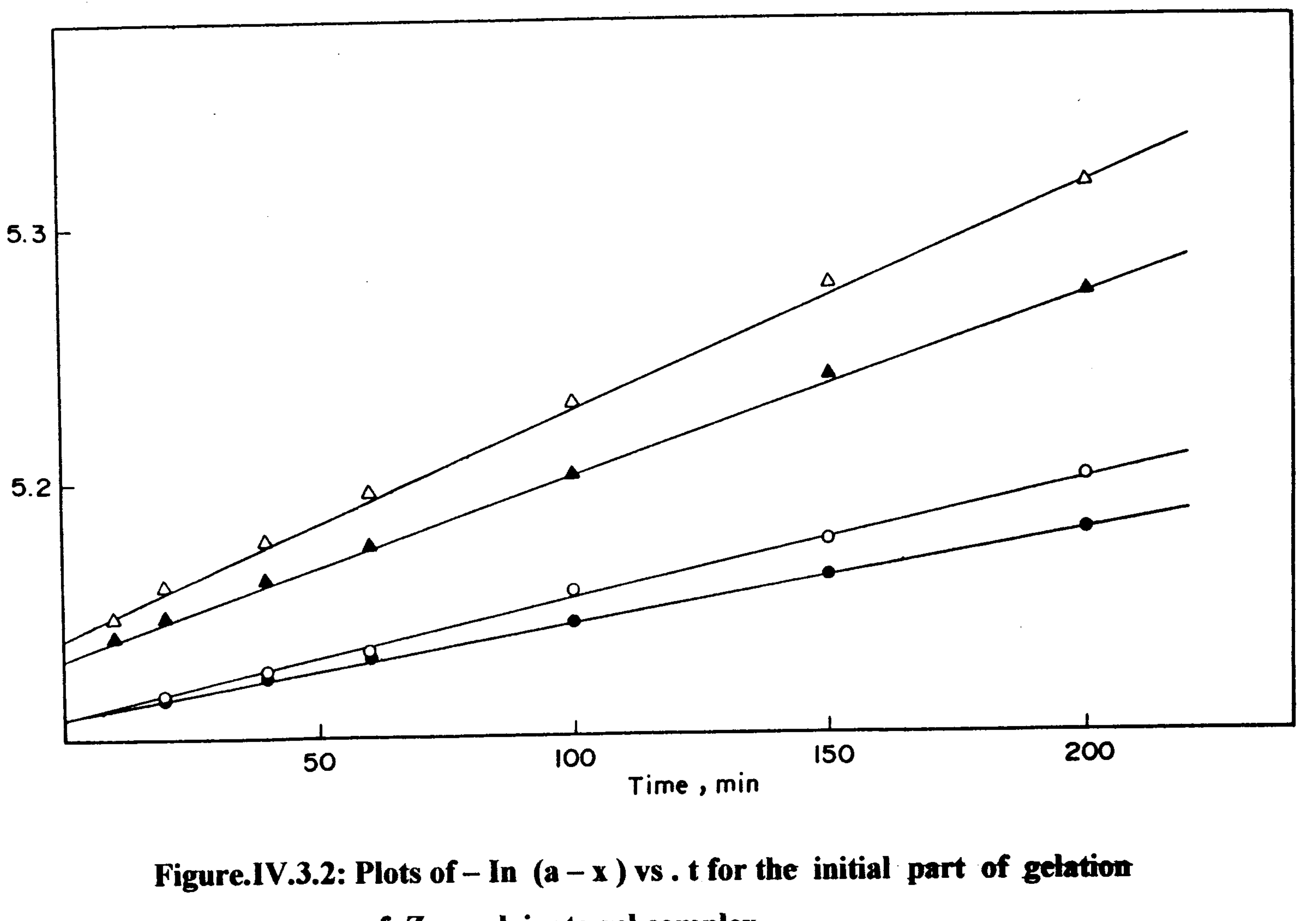


Figure.IV.3.2: Plots of – ln (a – x) vs . t for the initial part of gelation of Zn – alginate gel complex .

[Alg] = 5 x 10^{-2}, [Zn^{2+}] = 6.2 x 10^{-3}M.

[●]:35, [○]:45 , [▲]: 55, [Δ]: 65 °C .

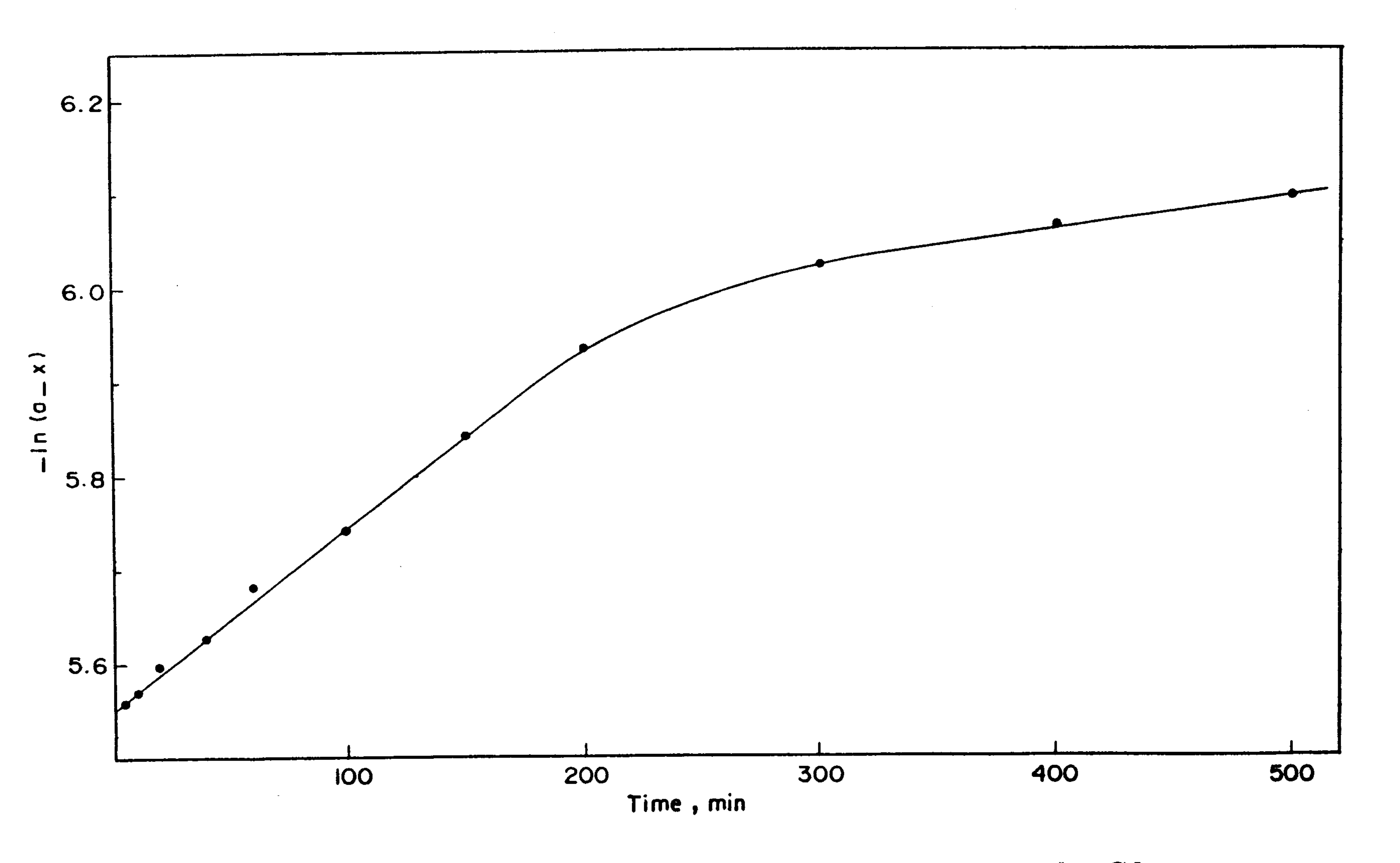


Figure.IV.3.3: Atypical pseudo – first – order plot of gelation for Cd-alginate gel complex

[Alg] = 5 x 10^{-2},[Cd^{2+}] = 4.0 x 10^{-3} M at 45°C .

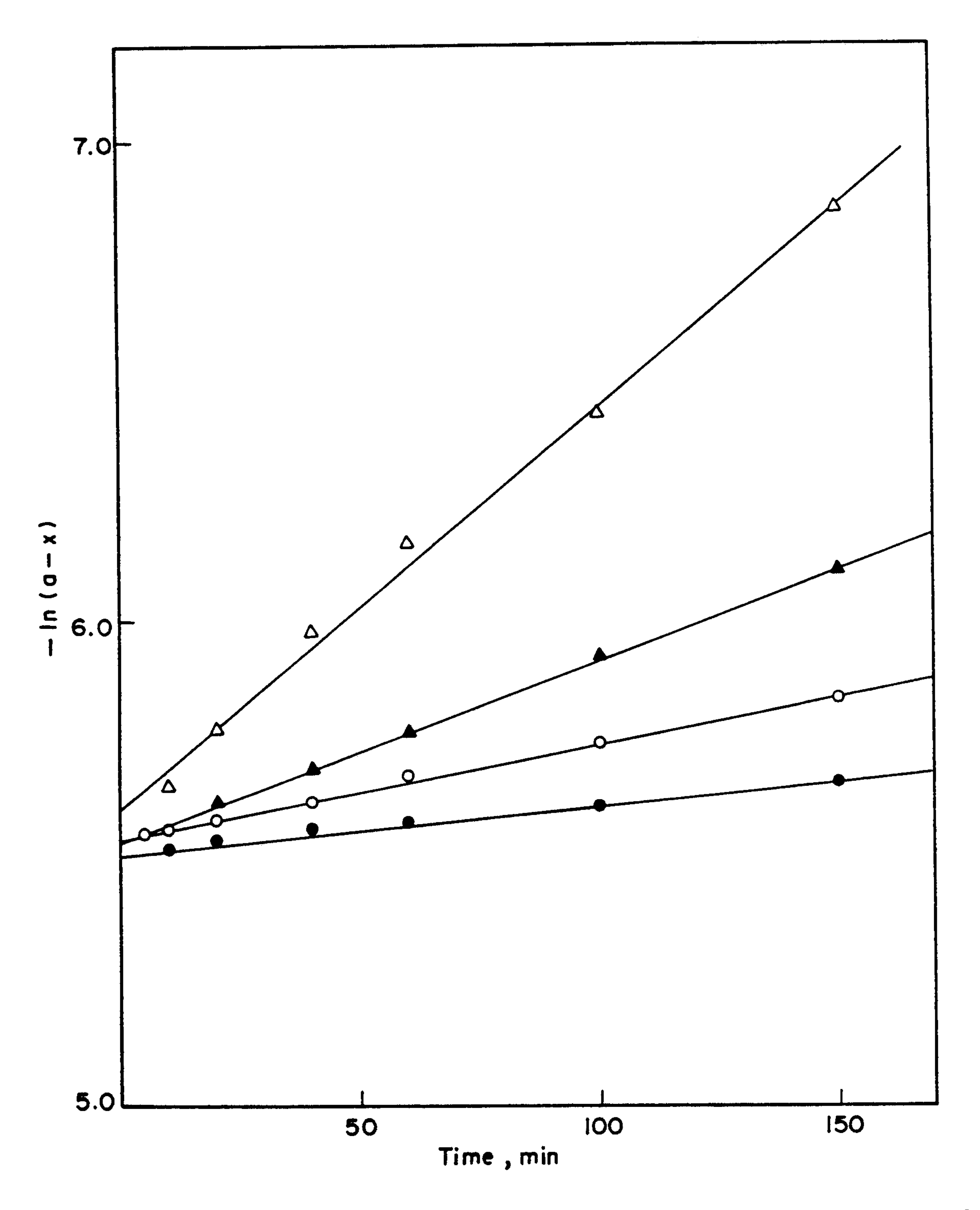


Figure.IV.3.4: Plots of− ln (a−x) vs . t for the initial part of gelation of Cd-alginate gel complex .

[Alg] = 5 x 10^{-2} , [Cd^{2+}] = 4 x 10^{-3} M .

[●]:35 , [○]: 45 , [▲]: 55 , [Δ]: 65 °C .

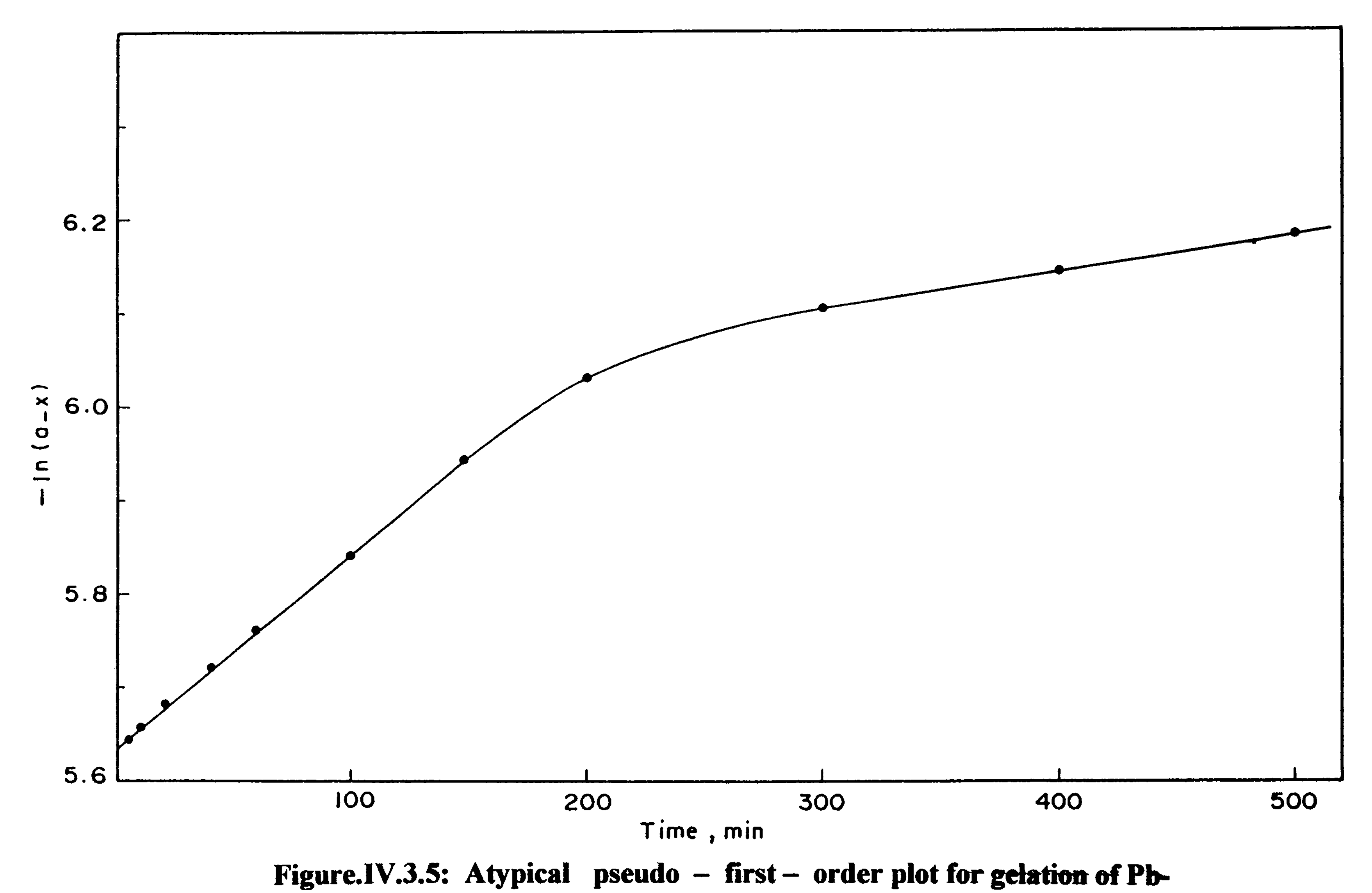


Figure.IV.3.5: Atypical pseudo – first – order plot for gelation of Pb-alginate gel complex.

[Alg] = 5 x 10^{-2} , [Pb^{2+}] = 3.85 x 10^{-3} M at 45 °C .

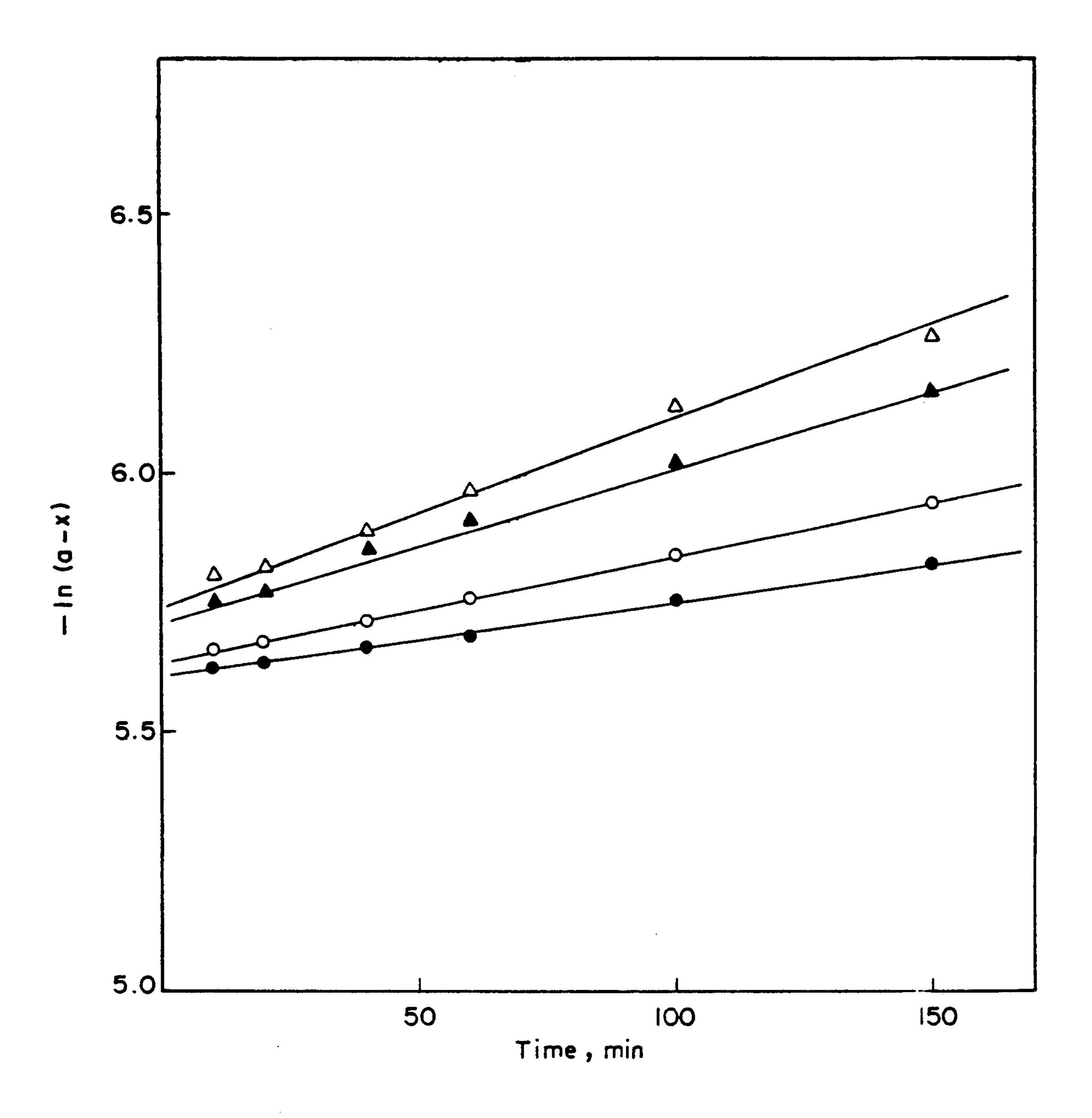


Figure.IV.3.6: Plots of – ln (a- x) vs . t for the initial part of gelation of Pb – alginate gel complex .

[Alg] = 5 x 10^{-2} ,[Pb^{2+}] = 3.85 x 10^{-3} M .

[●]:35, [○]: 45 , [▲]: 55 , [Δ]: 65°C .

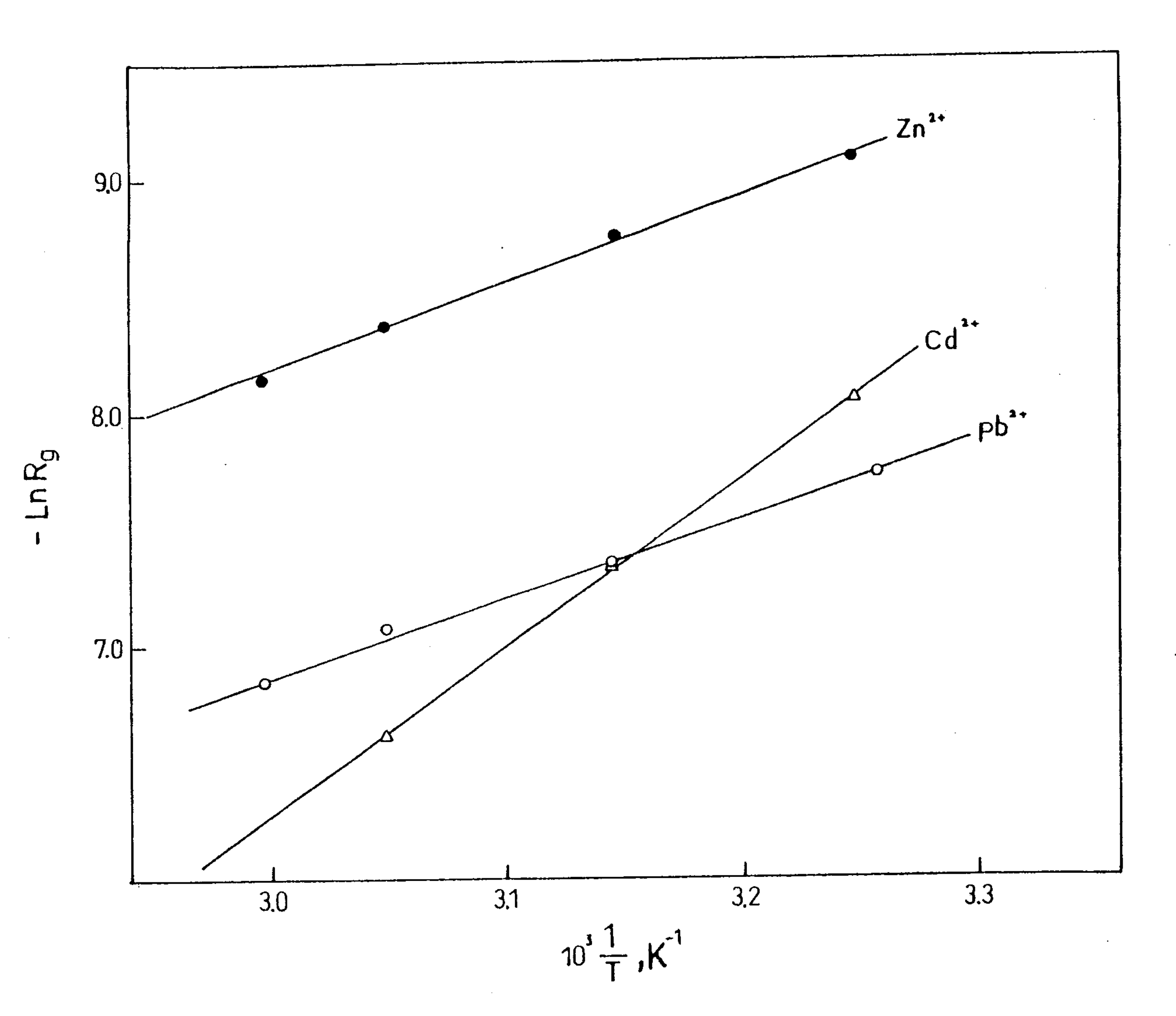


Figure.IV.3.7: Arrhenius plots for the fast initial stage gelation .

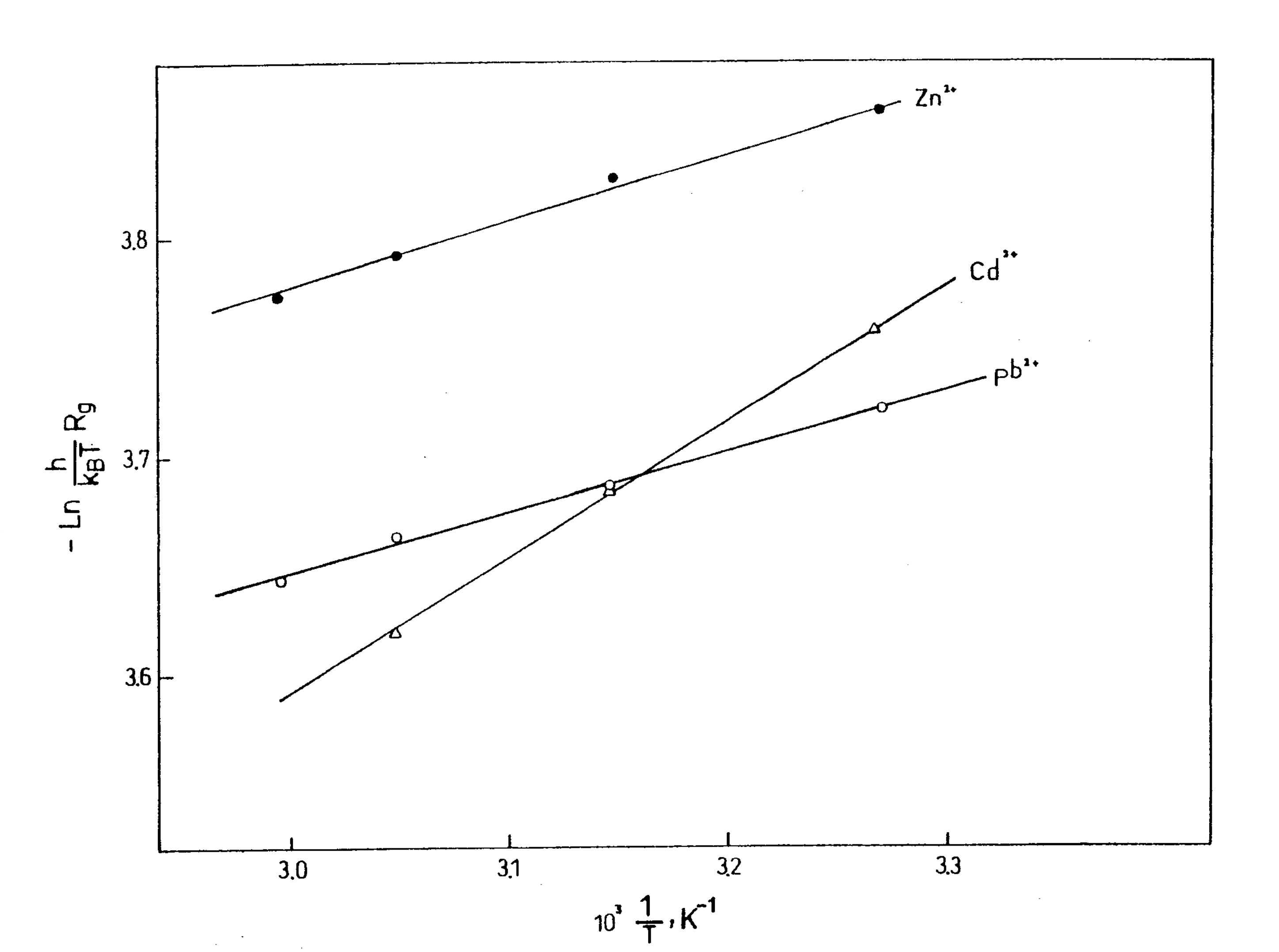


Figure.IV.3.8: Eyring plots for the fast initial stage of gelation.

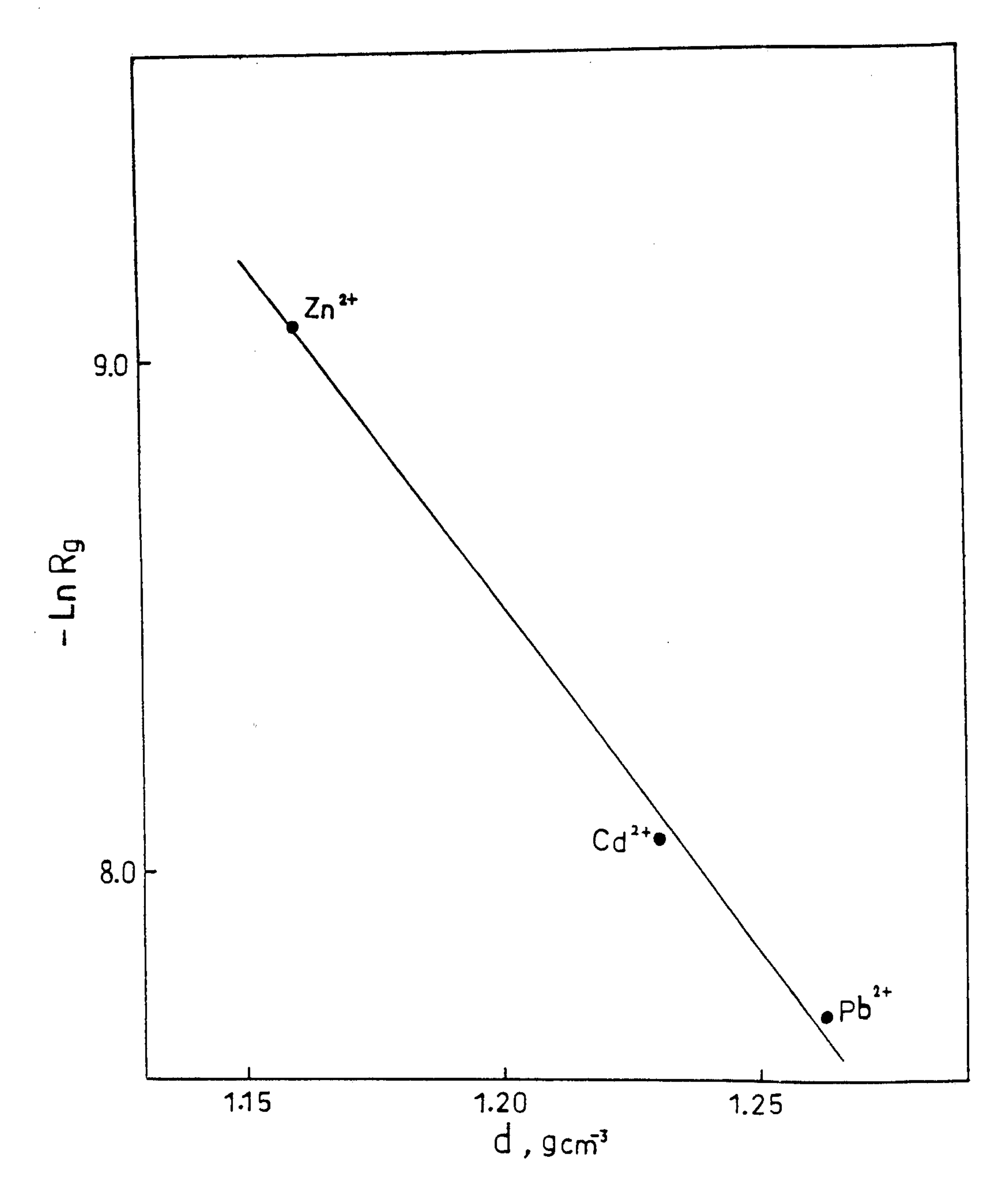


Figure.IV.3.9: Dependence of Gelation Rate on The Density of electrolytes.

[Alg $^-$] = 5 x 10^{-2}, [M^{2+}] = 4 x 10^{-3} Mat 35°C.

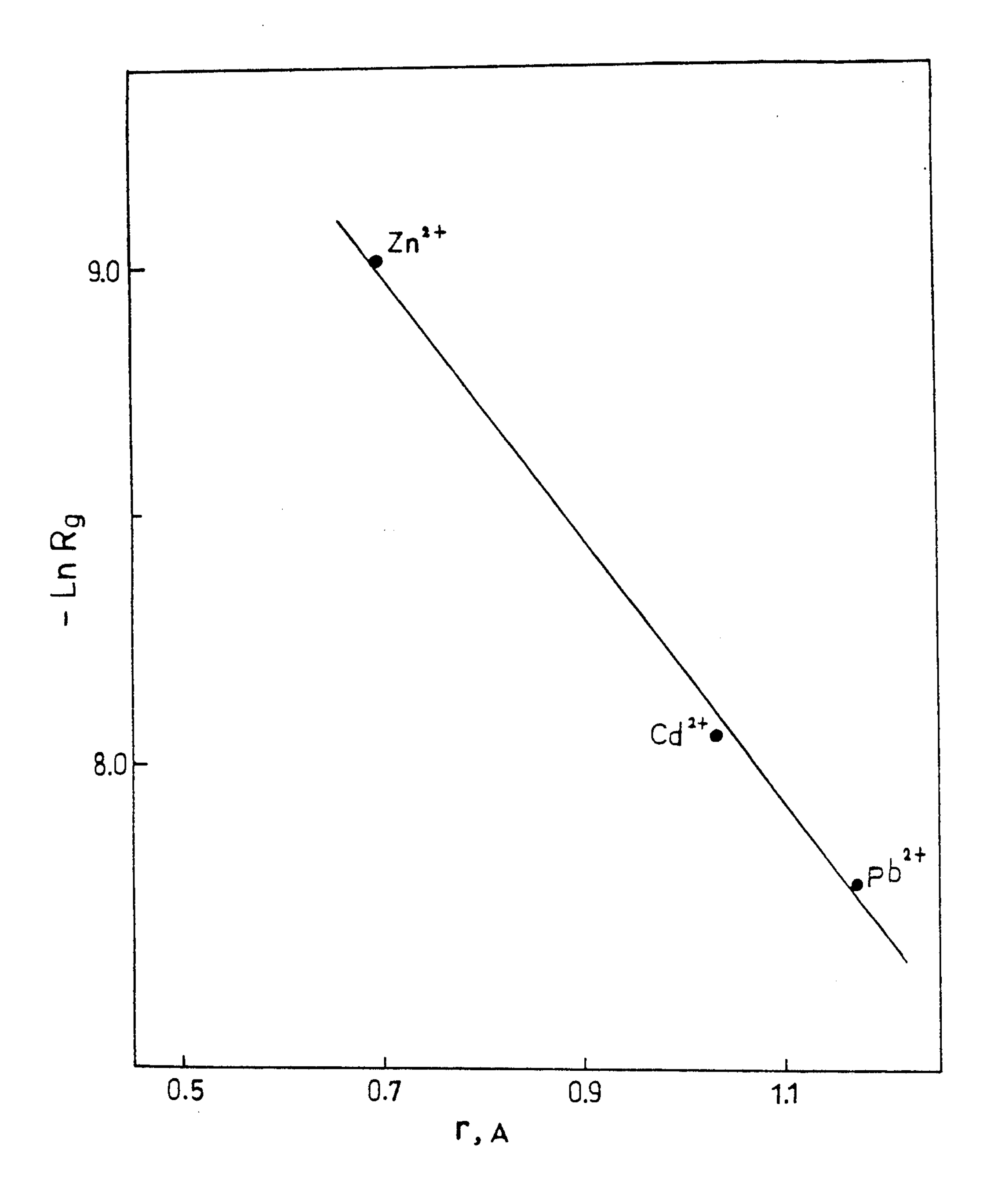


Figure.IV.3.10: Dependence of Gelation Rate on Ionic Radii. $[Alg^-] = 5x10^{-2}$, $[M^{2+}] = 4 \times 10^{-3}$ M at 45°C.

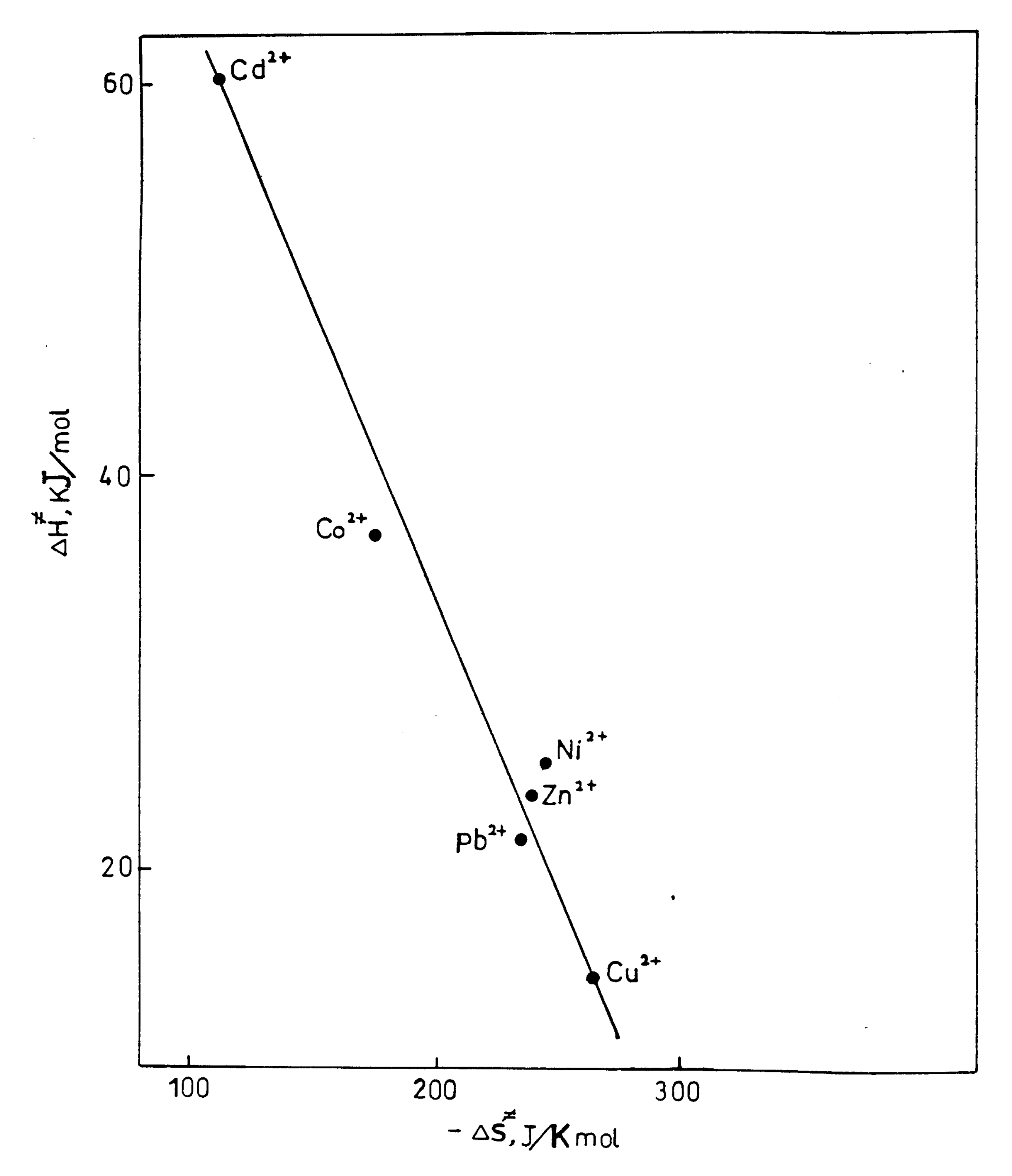


Figure.IV.3.11: Isokinetic Relationship for some Gelation Reactions.

Intramolecular

Intermolecular

Scheme (I) Chelation in divalent metal alginate complexes

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Caption of Tables

Chapter . II:

Chapter.III:

page

Caption of Figures

Chapter.II:

Chapter .IV:

page

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Summary and Conclusions

Summary and Conclusions

The work carried out in this thesis is presented in four main chapters .

The first chapter includes the introduction which contains a brief notes on the structure of sodium alginate polysaccharide . This besides a literature review on the published reports on alginates and its derivatives and the aim of the work .

The second chapter is concerned with the physical properties , characterization and morphology of metal – alginate ionotropic gel complexes .

It includes the preparation and standardization of metal ion electrolyte solutions . Also , the preparation of metal alginate in the form of gels , granules , membranes , columns and pellets are presented .

The physical properties such as viscosity , water content , mass , size and radius as well as the elasticity and transparency mechanical properties were investigated and discussed .

The characterizations of these metal alginate ionotropic gels such as the elemental analysis , X – ray diffraction patterns and FTIR are presented .

The stretching vibrations υ_a and υ_{as} of OCO groups as well as υ_{OH} were found to shift to lower frequencies and became more broader than that of alginates . This indicates that both COOH and OH functional groups of alginate macromolecule are shared in the chelation for these metal alginate complexes .

Moreover the optical and electromicroscopic investigations for these gel complexes indicated that these gels having ordered structures morphology . Photomicrographs of the various gel complexes are presented .

The third chapter involves a kinetic studys on Cd (II) , Sn (II) , Hg (II) and Pb (II) metal alginate gel complexes in the form of pellets . The rate constants of exchange between the sodium and metal counterions have been measured by the method of droplet – density change . The thermodynamic parameters for gelation were calculated from the temperature dependence of the rate constants of gel growth and are tabulated .

It has been found that as an alginate sol droplet gets in contact with an electrolyte solution of a divalent metal ion , a primary membrane is formed around the droplet at the interface between the electrolyte solution and the alginate sol . The droplet floats just below the electrolyte surface for a certain period of time called the relaxation time which is characterized for each metal ion electrolyte . After the relaxation time interval has elapsed , the droplet starts to sink into the electrolyte solution with an appreciable velocity which has been measured .

The diffusion factors affected the kinetics of sol – gel transformation , relaxation time and velocity of acceleration of the falling droplets were discussed . A mathematical treatment for the diffusion controls was proposed , examined and discussed .

The forth chapter presents a kinetic study on sol – gel transformation between alginate macromolecule sol and Zn (II) , Cd (II) and Pb (II) metal ions using the change in metal ion concentration technique . Pseudo first – order plots showed that the gelation reactions proceed through two distinct stages . The initial period was found to be relatively fast , followed by a slow step at the final stages . The results showed that the sol – gel

transformation process is first – order in both of the reactant concentrations and is second – overall gelation kinetics .

The kinetic parameters were evaluated from the dependence of the gelation rate constants on temperature using both Arrhenius and Eyring relationships and are tabulated along with that of other gelation reactions . The results showed that all these sol – gel transformations follow similar gelation mechanism and the rate constants lie in the same order of magnitude .

A consistent mechanism for sol – gel transformation processes the good agreement with the kinetic results was suggested and discussed .

Moreover , a geometrical model structure for chelation between the interdiffused metal ions and the carboxylate and hydroxyl groups of alginate macromolecule is suggested .